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Contents

	Page
The Alkaloids of <i>Lycopodium</i> Species. V. <i>Lycopodium obscurum</i> L.—R. H. F. Manske and L. Marion - - -	53
The Synthesis of Possible Degradation Products of Metathebainone. I.—H. L. Holmes and L. W. Trecoy - - -	56
Fibre Structure in Dispersions of Soap in Mineral Oil—W. Gallay, I. E. Puddington, and J. S. Tapp - - -	66
Low Temperature Saponification in Anhydrous Systems—W. Gallay and I. E. Puddington - - -	76
The Recrystallization of Sodium Soaps in Mineral Oils—W. Gallay and I. E. Puddington - - -	90
The Effect of High Shearing Stresses on Recrystallization of Sodium Soaps in Mineral Oils—W. Gallay and I. E. Puddington - - -	103

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VOL. 22, SEC. B.

MAY, 1944

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THE ALKALOIDS OF *LYCOPODIUM* SPECIES

V. *LYCOPODIUM* *OBSCURUM* L.¹

BY RICHARD H. F. MANSKE² AND LÉO MARION²

Abstract

Lycopodium obscurum var. *dendroideum* (Michx.) D.C. Eaton has yielded two apparently new alkaloids in addition to the known lycopodine and obscureine and to alkaloid L13 also found in *L. tristachyum*. One of these, alkaloid L16, is isomeric with lycopodine and with alkaloid L13, while the second, alkaloid L17, is best represented by $C_{18}H_{27}O_3N$. Nicotine is not present in tangible quantities.

Lycopodium obscurum var. *dendroideum* (Michx.) D. C. Eaton is the common variety of *L. obscurum* L. in the region from Newfoundland to North Carolina and northward. The variety here cited is not clearly distinct but is said to pass in imperceptible stages into the type species. Nevertheless the plant now examined is well representative of the varietal form and was kindly identified as such by Dr. H. Senn, Division of Botany, Central Experimental Farm, Ottawa. All the material was collected in woods near the left bank of the Ottawa River some fifty miles upstream from Ottawa. The exact identification of the source of the plant is now given because in a future communication dealing with *L. clavatum* L. the authors will have occasion to lay stress on the geographical source as a factor in the nature of the contained alkaloids. Most of the plant material was collected in July, but smaller collections were made in August and September.

The total alkaloid content was rather meagre but it has nevertheless been possible to isolate five alkaloids. Chief of these is lycopodine, followed by obscureine (L6) (3), which occurs in relatively larger quantities in the alkaloids of this plant than in those of other species so far examined.

The remaining alkaloids were obtained crystalline only in the form of their perchlorates. Two of these (alkaloids L13 and L16) yielded analytical figures that indicate that they are isomeric with lycopodine. The free bases, however, did not crystallize and seeding with lycopodine did not induce crystallization. Alkaloid L13 is identical with the base previously reported as occurring in *L. tristachyum* (4). The third (alkaloid (L17) which, together with alkaloid L16 appears to be new, is best represented by $C_{18}H_{27}O_3N$. It differs empirically from alkaloid L2 (2) from *L. flabelliforme* by having one oxygen substituted

¹ Manuscript received December 27, 1943.

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1191.

² Chemist.

for two hydrogens, and is another member of the rapidly growing series of lycopodium alkaloids with 18 carbon atoms. With two exceptions only, alkaloid L15 (4) and an alkaloid isolated from a mixture designated as L9 (3), which contain 20 carbon atoms, all the other alkaloids isolated by the authors appear to have 16 carbon atoms. On this basis it may be permissible to question the formula $C_{17}H_{25}ON_2$ of Deulofeu and De Langhe (1) for a new alkaloid, sauroxine, isolated from *L. saururus*. Actually, the analytical figures that they record agree somewhat better with $C_{16}H_{24}ON_2$. (Calc.: C, 73.85; H, 9.23; N, 10.77%. Found: C, 73.88; H, 9.29; N, 10.27%.)

Experimental

There was available a total of 38.2 kg. of dried and ground material. The total purified base (2) was distilled and two fractions were collected boiling at 160 to 172° C. (2 mm.) and 172 to 210° (2 mm.) respectively. The temperatures are those of the air-bath surrounding the distillation tube.

Lycopodine

The first fraction, which weighed 25 gm., crystallized readily and consisted for the greater part of lycopodine. It was dissolved in methanol and treated with 60% aqueous perchloric acid until the mixture was just acid to Congo red. The lycopodine perchlorate that separated was filtered, washed with methanol, and then with ethyl acetate. It weighed 31 gm. and melted at 281° C.*

Alkaloid L16

The filtrate from the lycopodine perchlorate was evaporated *in vacuo* and the residual thick syrup dissolved in acetone. The solution was again evaporated to a thick syrup and extracted with successive portions of anhydrous ether until neither solvent nor moisture was removed. The pasty residue was left in contact with dry ethyl acetate, and the crystalline material that separated in the course of several days was filtered off and washed with ethyl acetate containing a little acetone. The solid was then extracted with several successive portions of hot acetone (the insoluble portion consisted of lycopodine perchlorate) and the concentrated extract treated with ethyl acetate. The crystals thus obtained were recrystallized twice more from acetone-ethyl acetate; they then consisted of colourless prisms melting sharply at 221° C. Found: C, 55.51, 55.50; H, 7.79, 7.84; N, 4.08%. Calc. for $C_{16}H_{25}ON$. $HClO_4$: C, 55.25; H, 7.48; N, 4.03%.

Alkaloid L13

The higher boiling fraction (b.p. 172 to 210° (2 mm.)) weighed about 3.0 gm. It was dissolved in methanol and acidified with perchloric acid. Ethyl acetate was added until the incipient turbidity just disappeared on mixing. The perchlorate that then separated proved to be that of lycopodine. The filtrate from the lycopodine perchlorate was evaporated to a thick syrup,

* All melting points are corrected.

treated with hot ethyl acetate and sufficient acetone to yield a clear solution. In the course of several days a sparingly soluble salt separated; it was recrystallized a number of times from methanol-acetone. It then melted sharply at 272° C. either alone or in admixture with the perchlorate of alkaloid L13 isolated from *L. tristachyum* (4). Found: C, 55.36, 55.01; H, 7.48, 7.46; N, 4.19, 4.09%. Calc. for $C_{16}H_{25}ON \cdot HClO_4$: C, 55.25; H, 7.48; N, 4.03%.

Alkaloid L17

The mother-liquors from all of the above fractions were combined and the regenerated bases redistilled. The fraction boiling at 151° C. (1 mm.) yielded a perchlorate that was sparingly soluble in acetone. The salt was recrystallized several times from methanol-ethyl-acetate; it then consisted of brilliant large plates that began to darken slightly at 282 to 285° C. and became completely liquid at 296° C. Found: C, 53.22, 53.84; H, 7.04; 7.02; N, 3.57, 3.64%. Calc. for $C_{18}H_{27}O_3N \cdot HClO_4$: C, 53.28; H, 6.91; N, 3.45%.

Obscurine

The undistilled residue from the first distillation was dissolved in dilute aqueous oxalic acid and the filtered solution exhausted with ether. The solution was then basified with ammonia and shaken with a large volume of ether. The washed ether extract during evaporation deposited about 2.0 gm. of obscurine, which after recrystallization from chloroform-methanol, melted sharply at 282° C. either alone or in admixture with a specimen from *L. annotinum* (3).

It may be added that the odour of nicotine was detectable in the lower boiling fraction but there was not sufficient present to yield an identifiable picrate.

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THE SYNTHESIS OF POSSIBLE DEGRADATION PRODUCTS OF METATHEBAINONE. I.¹

BY H. L. HOLMES² AND L. W. TREVOY³

Abstract

The method of Crowley and Robinson (5) for the synthesis of 6-methoxy-3,4-dihydro-2-naphthoic acid has been modified to provide an improved and general method for the synthesis of 3,4-dihydro-2-naphthoic acids. The 7-methoxy-3,4-dihydro-2-naphthoic acid and its ethyl ester have been shown to react with butadiene and 2,3-dimethylbutadiene to give 3-methoxy-5,8,9,10,13,14-hexahydrophenanthrene-14-carboxylic acid and its 6,7-dimethyl derivative. The relationship of these hydrophenanthrenes to possible degradation products of morphine and metathebainone has been discussed. An unsuccessful attempt was made to lengthen the C₁₄-chain by converting the carboxyl group to an aldehyde group by the Rosenmund method followed by condensation with malonic acid. The projected conversion failed in the first stage.

Introduction

Elucidation of the structure of morphine and the related alkaloids, codeine and thebaine, by degradative methods, has attracted the attention of organic chemists for more than 60 years. During that time it has been established that morphine is a hydrophenanthrylene oxide derivative containing two hydroxyl groups, an ethylenic double bond and a -CH₂-CH₂-N-CH₃ chain. The C₃ hydroxyl is phenolic while that at C₆ is alcoholic in nature. With the ethene assigned to the position Δ^{7,8} (10) only the location of the ethanamine chain remains in doubt. The oxidation of codeine, the C₃-methyl ether of morphine, to hydroxycodeine by Ach and Knorr (1), followed by Pschorr's (12, 13) characterization of the methine base as a ketone, limited the attachment of the nitrogen atom to either C₉ or C₁₀. Although the carbon end of the ethanamine chain has been tentatively assigned by various workers to C₅ or C₈, Gulland and Robinson (10) considered that this linkage should be to C₁₃ to account for the elimination of the nitrogen chain upon aromatization of the hydrophenanthrene nucleus. Moreover, the Beckmann rearrangement of codeinone oxime and the subsequent degradation (17) of the isoxime lends credence to Formula I, proposed by Gulland and Robinson, for morphine. Finally, it has been shown that thebaine is the enol methyl ether of the ketone, codeinone.

There have been numerous degradations of morphine and its derivatives, codeine and thebaine, to partially or fully aromatic phenanthrenes accompanied by the migration or loss of the ethanamine chain. The structure of

¹ Manuscript received December 14, 1943.

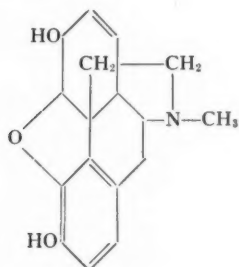
Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask., based on a thesis submitted by L. W. Trevoy to the Committee on Graduate Studies in partial fulfilment of the requirements for the degree of Master of Arts, April, 1943.

² Assistant Professor of Chemistry.

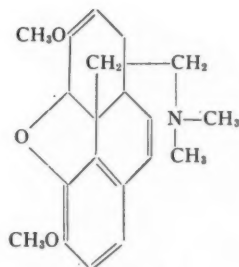
³ Graduate student and holder of a Bursary under the National Research Council of Canada, 1941-1942, and a Studentship, 1942-1943.

most of these phenanthrenes has been established from analytical data and confirmed by synthesis following the general method of Pschorr (14, 15). Contrasted with this, there have been but few attempts to degrade morphine or its derivatives to simpler hydrophenanthrenes that might be synthesized. All these attempts have fallen short of their goal owing to anomalous reactions.

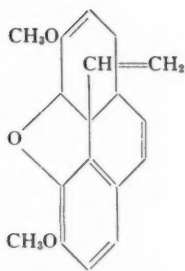
Cahn (3) attempted to degrade dihydrothebaine to 3,4-dimethoxy-13-ethyl-octahydrophenanthrene. He successfully converted the methiodide of dihydrothebaine methine (II) to 6-methoxy-13-vinyltetrahydromethylmorphenol (III) with amyl alcoholic potassium hydroxide, and the enol methyl ether was then hydrolysed with hydrochloric acid. The catalytic reduction of 6-keto-13-vinylhexahydro-methylmorphenol (IV) over platinized charcoal yielded 6-keto-13-ethyloctahydromorphol-3-methyl ether (VI), of Wieland and Kotake (22) by reductive cleavage of the oxide bridge of (V) with aluminum amalgam, but all attempts to methylate the weakly phenolic C₄-hydroxyl (18) failed and reduction of the C₆-ketone group yielded an oily product. However, it would appear that the 9,10-dihydro derivative of 6-methoxy-13-vinyltetrahydromethylmorphenol (III) should give 6-keto-octahydromethylmorphenol-13-carboxylic acid (VII) upon oxidation of the vinyl group followed by hydrolysis of the enol ether.



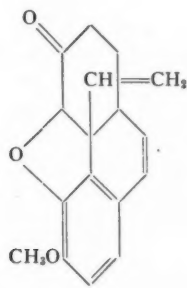
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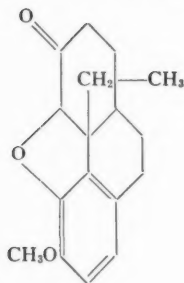
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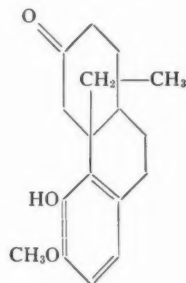
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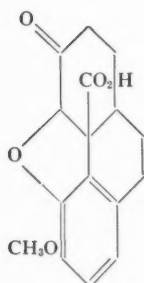
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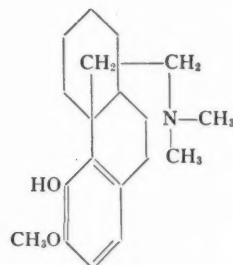
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VI



VII

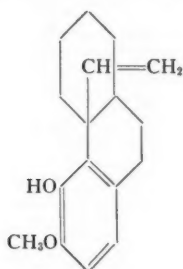


VIII

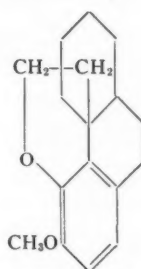
Speyer and Koulen (20) pursued a different course for the preparation of 3,4-dimethoxy-13-ethyloctahydrophenanthrene. These workers attempted to prepare dihydro-desoxytetrahydro- α -methylmorphimethine (VIII) by replacing the C₆ hydroxyl group of tetrahydro- α -methylmorphimethine by a chlorine atom followed by the reductive elimination of the chlorine atom and cleavage of the oxide bridge with sodium amalgam. Cahn (2) demonstrated that this methine base (VIII) contains either a $\Delta^{5,6}$ - or a $\Delta^{6,7}$ -ethylenic grouping. He also showed that, although the methiodide of this methine base readily lost trimethylamine in boiling alkali solution, the nitrogen-free product was not the expected 13-vinyloctahydromethylmorphol (IX) since it was insoluble in alkali and could be neither methylated nor acetylated. It probably has the ether structure*, X.

The corresponding methine from metathebainone would hardly be expected to undergo this anomalous ring closure, for a seven ring would then result. The C₁₄-methine corresponding to (VIII) has not been prepared but tetrahydrodesoxymetacodeine (XI) has been prepared by Small and Meitzner (19), and it would be expected that a series of two exhaustive methylations of the methyl ether of (XI) followed by oxidation of the vinyl group would lead to 3,4-dimethoxyoctahydrophenanthrene-14-carboxylic acid (XII).

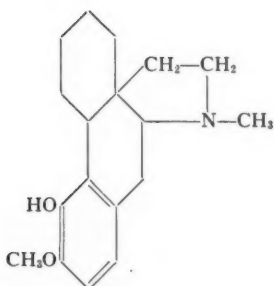
* The six-membered oxide ring is written in analogy with thebenone (19).



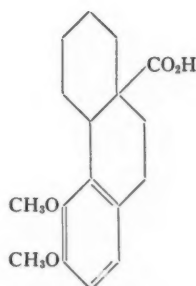
IX



X



XI



XII

With these degradations in mind the work presented in this paper was undertaken with two objectives: (i) the preparation of 3,4-dimethoxyoctahydrophenanthrene-14-carboxylic acid (XII) and (ii) the synthesis of 6-keto-octahydromethylmorphenol-13-carboxylic acid (VII). Although the work had to be discontinued short of completion, a synthesis of the 3-methoxy-analogue of (XII) has been developed and some work towards the synthesis of the acids (VII) and (XII) has been completed and will be presented in the second paper of this series.

The 3-methoxy-5,8,9,10,13,14-hexahydrophenanthrene-14-carboxylic acid and its 6,7-dimethyl derivative were obtained by the addition of 7-methoxy-3,4-dihydro-2-naphthoic acid, or its ethyl ester, to butadiene and to 2,3-dimethylbutadiene. The philodiene was prepared by cyclizing ethyl α -oxymethylene- γ -(4-methoxyphenyl)-butyrate in the same general way that Crowley and Robinson (5) obtained 6-methoxy-3,4-dihydro-2-naphthoic acid from ethyl α -oxymethylene- γ -(3-methoxyphenyl)-butyrate. The sulphuric acid mixture used by these workers led only to a sulphonated tarry material. However, if the strength of the acid was carefully controlled a satisfactory yield of the cyclized acid was obtained. The structure of the cyclized product was established by converting it to the 7-hydroxy-2-naphthoic acid of Ioffe and Fedorova (11) by dehydrogenation with sulphur, followed by demethylation with hydro-

bromic acid in acetic acid solution. The melting point of the hydroxy-acid as well as that of its acetate agreed with those recorded for these compounds.

The yield of addition product from the reaction of 7-methoxy-3,4-dihydro-2-naphthoic acid with 2,3-dimethylbutadiene (31%) was much better than that from the addition of this philodiene to butadiene (13%). Moreover, the yield and purity of the adduct from the acid and 2,3-dimethylbutadiene was superior to that obtained from the ethyl ester (18%). This agrees with the observations of Fieser and Holmes (8).

The hydrophenanthrene structure of the butadiene and 2,3-dimethylbutadiene adducts was demonstrated by dehydrogenation to 3-methoxyphenanthrene and its 6,7-dimethyl derivative. The 3-methoxyphenanthrene was characterized by its picrate and the 6,7-dimethyl derivative by the picrate, trinitrobenzene derivative, and quinone.

A single exploratory attempt was made to reduce the acid chloride of 3-methoxy-6,7-dimethylhexahydrophenanthrene-14-carboxylic acid to the corresponding aldehyde by the Rosenmund method, with a view towards lengthening the C₁₄ side chain. This experiment failed. However, in the light of the work of Campbell and Todd (4) there is hope that this reduction may be achieved.

Experimental*

7-Methoxy-3,4-dihydro-2-naphthoic Acid

This preparation was made in a 500 cc. round-bottomed flask fitted with a condenser, dropping funnel, and calcium chloride tube so arranged that material could be added dropwise through the condenser in the absence of water vapour. In this apparatus an ethereal solution of 31.3 gm. of isoamyl formate was added to a cold ethereal suspension of alcohol-free sodium ethylate (from 5.22 gm. of sodium). During the addition, the flask was shaken in an ice bath at intervals of from one to two minutes. When this addition was complete, an ethereal solution of 49.95 gm. of ethyl γ -(4-methoxyphenyl)-butyrate (7) was added dropwise through the condenser, with continued agitation of the flask in the cooling bath. The reaction mixture was maintained at 0° C. for several hours, and then allowed to stand at room temperature for four days. The deep red solution containing some suspended material was stirred into 500 gm. of ice and water. A mixture of γ -(4-methoxyphenyl)-butyric esters (ethyl and isoamyl; 14.5 gm., b.p. 190 to 210° C. (22 mm.)) was recovered by separating the ethereal solution and extracting the aqueous layer with two portions of ether. The aqueous solution of the sodium enolate of ethyl α -oxymethylene- γ -(4-methoxyphenyl)-butyrate was acidified with 2 *N* sulphuric acid and the oily formyl derivative extracted with three portions of ether. The ether extract was washed with water, then with saturated sodium bicarbonate and finally with saturated sodium chloride solution. After drying over anhydrous sodium sulphate, the ether

* All melting points were taken in an apparatus as described by E. B. Hershberg, *Ind. Eng. Chem. Anal. Ed.* 8: 312-313, 1936, and are corrected unless otherwise stated.

was flashed off and the isoamyl formate removed on a water bath at 22 mm. pressure.

The oily formylation product, which gave a violet ferric chloride coloration, was too sensitive to heat to purify by distillation so the impure material (34.5 gm.) was cyclized in a mixture of sulphuric and phosphoric acids. The oily reaction product was added dropwise to a vigorously stirred mixture of 133 cc. of phosphoric acid (sp. gr. 1.75) and 28 cc. of sulphuric acid (sp. gr. 1.832), which was cooled in an ice-salt bath to -10°C . The stirring was continued for two hours after the formylation product had been added, and then the mixture was poured into ice and water. The ethereal extract of the viscous oil from the reaction was carefully washed free of acid with water and sodium bicarbonate solution and dried over anhydrous sodium sulphate. The mixture, 17.1 gm., of ethyl and isoamyl esters of 7-methoxy-3,4-dihydro-2-naphthoic acid boiled over a range, 175 to 185°C . (2 mm.).

The esters were saponified and 10.6 gm. of 7-methoxy-3,4-dihydro-2-naphthoic acid was recovered. The over-all yield of this acid melting at 147 to 148°C . was 23.1%. The acid crystallized from ethyl alcohol in rectangular plates and after three crystallizations melted at 149.5 to 150°C . The sodium salt crystallized from aqueous sodium bicarbonate solution as rosettes of needles. Calc. for $\text{C}_{12}\text{H}_{12}\text{O}_3$: C, 70.57; H, 5.92%; neut. equiv., 204.2. Found: C, 70.23; H, 6.07%; neut. equiv., 206.3.

7-Methoxy-2-naphthoic Acid

The 7-methoxy-3,4-dihydro-2-naphthoic acid was dehydrogenated with sulphur. The acid (0.580 gm.) and 0.090 gm. of sulphur were heated in a von Braun flask at 240°C . until hydrogen sulphide was no longer evolved (about 45 min.). The dehydrogenation product, a pale yellow solid, was recovered by distillation under a pressure of 22 mm. It was dissolved in ethyl alcohol from which 0.33 gm. (58%) of the acid crystallized in rosettes of needles. The pure 7-methoxy-2-naphthoic acid melted at 195 to 196°C . and dissolved readily in sodium bicarbonate solution from which the sodium salt crystallized in long needles. Calc. for $\text{C}_{12}\text{H}_{10}\text{O}_3$: C, 71.27; H, 4.99%; neut. equiv., 202.2. Found: C, 71.21; H, 5.35%; neut. equiv., 205.3.

7-Hydroxy-2-naphthoic Acid

A solution of 7-methoxy-2-naphthoic acid (0.15 gm.) in 0.5 cc. of acetic acid was refluxed with 3 cc. of constant boiling hydrobromic acid. While the solution was still hot, water was added until a slight turbidity appeared and the product began to crystallize. The hydroxy-acid, when collected and dried, was somewhat coloured, so an alcoholic solution of the acid was decolorized twice with Norit. When the filtrate was concentrated the acid crystallized in clusters of pale yellow needles, m.p. 269 to 270°C . (uncorr.), 274 to 275°C . (corr.). The yield was 0.080 gm. (57%). Ioffe and Fedorova (11) reported that 7-hydroxy-2-naphthoic acid melted at 268 to 269°C . (uncorr.) and that the acetate melted at 209°C . (uncorr.).

The acetylation of 7-hydroxy-2-naphthoic acid was effected by heating 0.060 gm. of the acid with 1 cc. of acetic anhydride containing 0.03 gm. of fused potassium acetate. While the reaction mixture was still hot, water was cautiously added through the condenser to decompose the acetic anhydride, and when cold, the acetate crystallized from the acetic acid in glistening white plates. After repeated recrystallization from dilute acetic acid, the acetate melted at 208 to 209° C. (uncorr.), 210.5 to 211.5° C. (corr.).

3-Methoxy-5,8,9,10,13,14-hexahydrophenanthrene-14-carboxylic Acid

A solution of 4.93 gm. of 7-methoxy-3,4-dihydro-2-naphthoic acid in 4 cc. of sodium-dry toluene was heated in a sealed tube with a slight excess of butadiene for 100 hr. at 170° C. The reaction mixture was twice refluxed with 10% sodium hydroxide and on acidification of the alkaline solution with hydrochloric acid, 3.68 gm. of mixed acids was recovered. The 3-methoxyhexahydrophenanthrene-14-carboxylic acid was separated from the philodienic by fractional crystallization from aqueous ethanol. This adduct crystallized from benzene and petroleum ether in plates, and when collected and dried it melted at 126 to 127° C. The acid was soluble in sodium carbonate solution, in which solution it decolorized potassium permanganate instantly. Calc. for $C_{16}H_{18}O_3$: C, 74.40; H, 7.03%; neut. equiv., 258.3. Found: C, 74.67; H, 7.05%; neut. equiv., 260.8.

3-Methoxyphenanthrene

The 3-methoxyhexahydrophenanthrene-14-carboxylic acid (0.080 gm.) was dehydrogenated, over palladium precipitated upon barium sulphate (16), to 3-methoxyphenanthrene at a temperature of 340 to 350° and 16 cc. of hydrogen (theory, 21 cc.) was collected. The dehydrogenation product was isolated as the picrate, which, when purified from alcohol, gave orange red needles that melted with some previous softening at 123 to 124° C.

The picrate was decomposed with ammonia and the 3-methoxyphenanthrene taken up in ether. When the solvent was removed the recovered product crystallized from alcohol and melted at 48 to 49° C. Owing to the limited amount of material recovered, it was not possible to obtain the 3-methoxyphenanthrene in a high state of purity.

Ethyl 3-Methoxy-6,7-dimethyl-5,8,9,10,13,14-hexahydrophenanthrene-14-carboxylate

A solution of 7.4 gm. of ethyl 7-methoxy-3,4-dihydro-2-naphthoate in 5 cc. of sodium-dry toluene was heated with 3.0 gm. of 2,3-dimethylbutadiene in a sealed tube at 170° for 72 hr. The residual oil, after removal of the toluene, was distilled under vacuum. The unchanged ester was separated from the ester-adduct by refluxing the distillate with 15% sodium hydroxide solution and then extracting the residual ester-adduct with ether. After removal of the ether, 1.8 gm. (18%) of ethyl 3-methoxy-6,7-dimethylhexahydrophenanthrene-14-carboxylate was recovered; it boiled at 187° C. (2 mm.).

Acidification of the alkaline solution led to a recovery of 1.1 gm. of 7-methoxy-3,4-dihydro-2-naphthoic acid.

3-Methoxy-6,7-dimethyl-5,8,9,10,13,14-hexahydrophenanthrene-14-carboxylic Acid

A. A solution of 4.7 gm. of 7-methoxy-3,4-dihydro-2-naphthoic acid in toluene was added to 5.0 gm. of 2,3-dimethylbutadiene under conditions similar to those for the addition of the ester to 2,3-dimethylbutadiene.

The reaction product, consisting of a mixture of the starting acid and the acid-adduct, was esterified by the Fischer-Speier method. The ester mixture boiled over a range from 165 to 188° C. (2 mm.). On cautious saponification the ethyl 3-methoxy-6,7-dimethylhexahydrophenanthrene-14-carboxylate was unaffected by the 10% sodium hydroxide solution, for it was recovered in ether, dried, and distilled. After removal of the solvent, 3.3 gm. (46%) of the ester, which boiled at 187° C. (2 mm.), was collected. From the alkaline solution 0.68 gm. of 7-methoxy-3,4-dihydro-2-naphthoic acid was recovered.

The ester adduct was saponified by refluxing with sodium ethylate (2.0 gm. of sodium in 30 cc. of absolute ethyl alcohol) for five hours. The material obtained by this method was difficult to purify, for after many crystallizations from ethanol, the acid, which crystallized in rosettes of colourless needles, when dried, melted at 132 to 133° C.

B. A solution of 12.5 gm. of 7-methoxy-3,4-dihydro-2-naphthoic acid in 10 cc. of dry toluene was heated at 180° C. for 72 hr. in a sealed tube with 6.5 gm. of 2,3-dimethylbutadiene. Upon cooling, some of the unreacted acid (5.3 gm.) crystallized in the sealed tube and was removed by filtration. The remaining unreacted philodine and the acid-adduct were extracted from the toluene solution by refluxing with 20% sodium hydroxide solution for five hours. The alkaline extract, after separation of the toluene layer, was acidified with hydrochloric acid and the carboxylic acid was collected, washed, and dried. To remove small traces of diene polymer the mixture of acids was dissolved in ethyl alcohol and filtered. When the alcoholic filtrate was concentrated and diluted with a small amount of water, the 3-methoxy-6,7-dimethylhexahydrophenanthrene-14-carboxylic acid crystallized in dense rosettes. The first crop of crystals combined with a second crop weighed 5.5 gm. (31.4%) and melted at 130 to 135° C. This impure acid was recrystallized from ethanol until a constant melting point of 137.5 to 138.2° C. was attained. Calc. for $C_{18}H_{22}O_3$: C, 75.49; H, 7.74%; neut. equiv., 286.3. Found: C, 75.43; H, 8.13%; neut. equiv., 287.2.

3-Methoxy-6,7-dimethylphenanthrene

A mixture of 1.8 gm. of ethyl 3-methoxy-6,7-dimethylhexahydrophenanthrene-14-carboxylate and 0.5 gm. of powdered selenium was heated to 310° C. in a salt bath, and after every eight hour interval, an additional 0.5 gm. of selenium was added. When cold, the dehydrogenated product was extracted in dry ether and refluxed with sodium. The ether was removed and the product was collected in a von Braun flask from which it was partially purified by vacuum distillation at 22 mm. pressure. The yellow distillate, which soon solidified, was purified by converting it to the picrate which crystallized from alcohol in bright red needles. The picrate, which melted at 182.5 to 183.5° C.,

was decomposed in ammonia and the 3-methoxy-6,7-dimethylphenanthrene recovered in ether. Recrystallization of the product from alcohol gave flat plates of 3-methoxy-6,7-dimethylphenanthrene that melted at 118 to 119° C. Fieser and Holmes (8) report that this product melted at 119 to 120° C.

The 3-methoxy-6,7-dimethylphenanthrene was further characterized as its trinitrobenzene derivative, m.p. 179 to 181° C. and by oxidation with chromic acid (21) to the quinone. The 3-methoxy-6,7-dimethylphenanthrene-quinone crystallized in long slender golden-brown needles from acetic acid, and melted at 224.5 to 225.5° C.

An Unsuccessful Attempt to Prepare 3-Methoxy-6,7-dimethyl-5,6,7,8,9,10,13,14-octahydro-14-phenanthraldehyde

The acid chloride of 3-methoxy-6,7-dimethylhexahydrophenanthrene-14-carboxylic acid was prepared by warming 6.7 gm. of the acid with 5.13 gm. of phosphorus pentachloride in a Claisen flask, equipped with a reflux condenser. The flask was gently heated to start the reaction and, after the violent reaction was over, the reaction mixture was again heated in a water bath to ensure complete reaction. The acid chloride distilled at 170 to 180° C. (3 mm.), yield, 3.5 gm.

The chloride was immediately dissolved in 100 cc. of sodium-dry toluene in a 500 cc. three-necked flask equipped with reflux condenser, a mercury-sealed stirrer, and an inlet tube for hydrogen, which extended below the surface of the toluene. After adding 1.0 gm. of palladium-barium-sulphate catalyst (16) and 2 drops of quinoline-sulphur poison, an oil bath surrounding the flask was heated to 135° C. and dry hydrogen was bubbled into the stirred solution. The escaping gas, after passing through a calcium chloride tube, was bubbled into 100 cc. of water containing phenolphthalein and 0.5 cc. of 1.328 *N*. sodium hydroxide solution.

Although three 1 gm. portions of catalyst were added there was no evidence that reduction had occurred even after boiling had continued for five hours.

3,4-Dihydro-2-naphthoic Acid

Forty-eight grams of ethyl γ -phenylbutyrate was condensed in the usual manner with 35.0 gm. of isoamyl formate in the presence of alcohol-free sodium ethylate (from 11.6 gm. of sodium). After standing for four days at room temperature the reaction mixture was poured into 1 litre of ice and water and the unreacted starting ester extracted in ether. The ethyl α -oxymethylene- γ -phenylbutyrate was recovered by acidifying the aqueous solution with dilute sulphuric acid and extracting the oily product in ether. The ethereal extract was thoroughly washed with water and saturated sodium bicarbonate solution and dried over sodium sulphate. The solvent was distilled and the excess isoamyl formate removed under vacuum, leaving an oily residue weighing 34.0 gm. The unpurified oxymethylene-derivative was cyclized in 50 cc. of sulphuric acid (sp. gr. 1.832) and 250 cc. of phosphoric acid (sp. gr. 1.75) under conditions similar to the previous cyclization experiments. The mixture of the ethyl and isoamyl esters of 3,4-dihydro-2-naphthoic acid distilled

at 138 to 148° C. (4 mm.). The mixed esters were saponified in 75 cc. of 10% sodium hydroxide solution containing 4 to 5 cc. of ethanol, and the alkaline solution while still hot was diluted with 100 cc. of water, decolorized with Norit, and acidified with dilute hydrochloric acid. The solid acid was collected on a Büchner funnel, washed free of hydrochloric acid and dried. The dry acid weighed 16.7 gm. (86%) and melted at 111 to 113° C. After two recrystallizations from petroleum ether (30 to 60° C.) the acid, which crystallized in dense prisms, melted at 118° C. Derick and Kamm (6) reported that this acid melted at 118.5° C.

β-Naphthoic Acid

An intimate mixture of 5.00 gm. of 3,4-dihydro-2-naphthoic acid and 1.00 gm. of sulphur in a von Braun flask was heated to 230 to 240° C. in a salt bath. In 40 min. the evolution of hydrogen sulphide had ceased and the odour of naphthalene could be detected. The dehydrogenation product was partially purified by distillation under a pressure of 2 mm. and the distillate soon solidified. The pale yellow solid (4.10 gm.) was dissolved in ethanol, decolorized with Norit, and finally crystallized from this solvent. The long needles of this acid, when dry, weighed 3.5 gm. (70%) and melted at 180.5 to 182.5° C.

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FIBRE STRUCTURE IN DISPERSIONS OF SOAP IN MINERAL OIL¹

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Abstract

The texture and other physical properties of soap dispersions in mineral oil, or lubricating greases, depend largely on the degree of dispersion of the soap. Calcium and aluminium soap dispersions yield in general a very short unctuous texture owing to the small size of the soap fibres in these systems. Sodium soap dispersions show a wide range of texture from a smooth to a very fibrous character, and this is related to the dimensions of the soap fibres in the dispersion.

A novel method of examination of these fibres is described, and this procedure is compared with other means. Data and photographs of soap fibres are shown.

The development of large fibres is discussed and the growth of fibres by orientation and overlapping of smaller fibrils is described. Evidence is adduced by micro-manipulator examination of soap and non-soap fibres in mineral oil. The effect of glycerol, present in greases manufactured from fats, is shown to be essential for the production of long fibres in ordinary practice, and this effect is ascribed mainly to the ability of oil to wet the soap in the presence of glycerol.

Introduction

The metallic soaps of fatty acids are virtually insoluble in mineral oils, and the two-phase systems obtained after heating suspensions of the soap in oil and cooling show a wide variation in physical properties. The texture ranges from a smooth unctuous paste to a rough, highly fibrous material, with any number of intermediate gradations. The degree of fibrous texture is known to be dependent on a number of factors, among which may be listed, (1) the metal of the soap, (2) the degree of unsaturation of the fatty acid, (3) excess acidity or alkalinity, (4) presence of certain added materials such as water and glycerol, (5) the viscosity of the oil, (6) the polarity of the oil as represented by its viscosity index, (7) the rate of cooling during manufacture, (8) the amount of agitation used during manufacture, etc. These soap-mineral-oil systems find application particularly as lubricating greases, and for this purpose the texture of the material is of particular importance. The ability of various greases to cling to metallic surfaces in gear lubrication, or to add a minimum of load in ball-bearing lubrication, or to ensure non-channelling characteristics for transmission lubrication is of first-rate importance in industrial use.

The present study is concerned with methods of examination of the soap fibres in such systems, the measurement of fibre dimensions, and an investigation of the mode of formation, structure, and physical properties of the

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fibres. The materials used were mainly various lubricating greases of commercial manufacture, but in some instances laboratory-prepared suspensions were examined for special purposes as noted.

Microscopic Examination of Fibre Structure

Attempts were first made at resolving the two-phase system with ordinary transmitted light but in most instances no inhomogeneity could be observed. Observation in dark field using a Cardioid condenser brought about only an unsatisfactory vague resolution of the fibres. Farrington and Davis (2) have described similar experiments using a dark field technique (Spot-Ring condenser), and have classified lubricating greases on the basis of fibre length as follows:

Classification	Fibre length, μ	Texture
Long fibre	100 or more	Fibrous, ropy
Medium fibre	10 - 100	Clinging, slightly rough
Short fibre	1 - 10	Slightly rough, short
Micro fibre	1 or less	Smooth, unctuous

Examination of the photomicrographs given by Farrington and Davis shows that the resolution obtained was rather vague, and comparisons are rendered somewhat difficult by lack of definite resolution. There is no doubt, however, that the texture is directly related to the length of fibre in the suspension.

In the present work, a greatly improved degree of resolution was obtained using transmitted polarized light, and large differences in fibre lengths could be readily distinguished by this means. It was observed, however, that the longer fibres were bent and curled, and therefore it was not possible to view one fibre along its whole length at one focused position. Changing the focus brought into view various positions of the same fibre. Fig. 1 shows a photomicrograph of a long-fibred sodium soap grease which appears to have short fibres for the above reason.

After a number of further trials, the following procedure was developed for the resolution of fibres in these systems. A small sample of the grease was gently shaken with ether in a test-tube and then transferred to a microscope slide with a minimum of working or mechanical disturbance. The grease was then washed by pouring several portions of fresh ether along the slide held in a sloping position. The extracted grease adheres well to the slide and the ether effects an extraction of oil and a separation of fibrils from the coarser fibre originally found in the grease by viewing in polarized light. This technique was shown to yield reproducible results on successive trials, and it provides a reliable means of evaluating comparatively the length of fibre in such systems. The method is applicable particularly to sodium soap dispersions. Figs. 2, 3, and 4 show examples of photomicrographs of

representative short, medium, and long-fibred sodium soap greases, obtained by the use of this technique. The effectiveness of the dry slide technique is strikingly shown in these figures.

Calcium soap dispersions in oil are known to yield smooth textures only. Our extraction method of slide preparation is not applicable to these dispersions because of agglomeration. Fig. 5 shows a photomicrograph of a typical calcium soap grease taken by transmitted polarized light.

Aluminium stearate dispersions in oil yield fibres so small that it has not been found possible to obtain any effective resolution by any method tried. Such systems can be obtained in two general forms, viz., amorphous and crystallized, depending on certain added agents and temperature. Using polarized light and a very powerful light source, no structure could be observed in the elastic or amorphous system, but extremely fine particles could be discerned in the grease containing crystallized soap. No structure could be seen in these greases in dark field using the slit ultramicroscope.

Dimensions of Fibres in Soap-Oil Systems

Measurements of the approximate length and diameter of the fibres in various lubricating greases were carried out. The samples were viewed with polarized light in the original condition, since measurements of length on samples prepared by our dry slide technique are difficult owing to entanglements of fibres. Table I shows some data obtained, each value being an average of a number of determinations.

TABLE I
DIMENSIONS OF SOAP FIBRES IN GREASES

Sample No.	Fibre length, μ	Fibre diameter, μ	Description
1	410	6 - 7	Long-fibred
2	330	4 - 9	Long-fibred
3	60	0.6 - 0.9	Medium-fibred
4	1 - 10	0.5 - 4	Short-fibred

It is noted that our measurements on samples viewed in polarized light correspond well to those of Farrington and Davis (2) made in dark field observations. These fibres are obviously gross structures and finer sub-structures are readily discernible in the microscope. The dry slide preparations showed approximately the same diameters as those in the original condition in the dispersion.

The qualitative measurement of fibre length in such systems is often carried out in commercial practice by feel, e.g., by quickly stretching a small sample between the fingers, or quickly lifting a small sample with a finger tip from the palm of the hand. A longer string-out can be obtained from systems

PLATE I

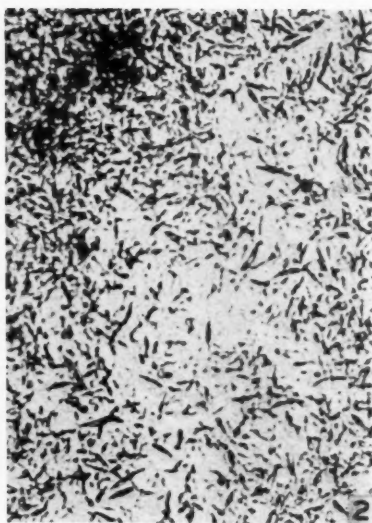


FIG. 1. Long-fibred sodium soap grease. Polarized light. $\times 135$. FIG. 2. Short-textured sodium soap grease, showing short soap fibres. Dry slide technique. Transmitted light. $\times 240$. FIG. 3. Medium-textured sodium soap grease, showing soap fibres of intermediate length. Dry slide technique. Transmitted light. $\times 240$.

PLATE II

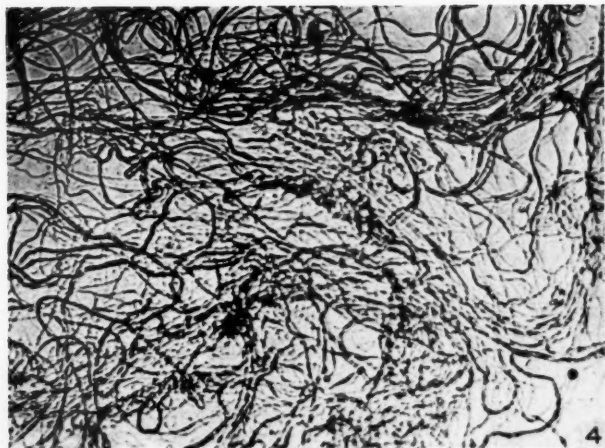


FIG. 4. Long-textured sodium soap grease, showing very long soap fibres. Dry slide technique. Transmitted light. $\times 220$. FIG. 5. Typical calcium soap transmission grease. Polarized light. $\times 65$. FIG. 6. Sodium soap grease showing orientated bands of soap fibres brought about by mechanical orientation. Polarized light. $\times 650$.

containing longer fibres owing to the greater overlapping obtained. This is discussed further in a later section.

An apparatus was constructed to measure this length of string-out in a standard manner, similar in principle to that described by Erbring (1). It consisted essentially of a small shallow container for the grease sample, and a motor-driven arrangement for raising and lowering continuously a glass rod above the sample. The rod penetrated to a definite standard depth into the grease on each stroke, and the length of stroke was sufficient to break the grease fibre, which was pulled by the rod from the sample on each upward stroke. It was found necessary to dilute the suspension to about 2% soap concentration in order to draw fibres of convenient length. An important feature of the apparatus is the contour of the end of the rod. After various trials, a hemispherical shape was adopted for most uniform results. The fibre length was established by adjusting the height of the stroke until the fibre just broke, and measuring this height by a suitable scale.

Fig. 7 shows the results in a comparison between hand evaluation of comparative fibre length and the relation shown by the apparatus described above. Twelve samples of lubricating greases of commercial manufacture were rated in order of fibre length by hand (personal classification) and by the apparatus (machine classification). The continuous line shows points of perfect agreement between the two methods. It is noted that the general agreement is good, 50% of the points falling on the line and the others equally distributed about the line.

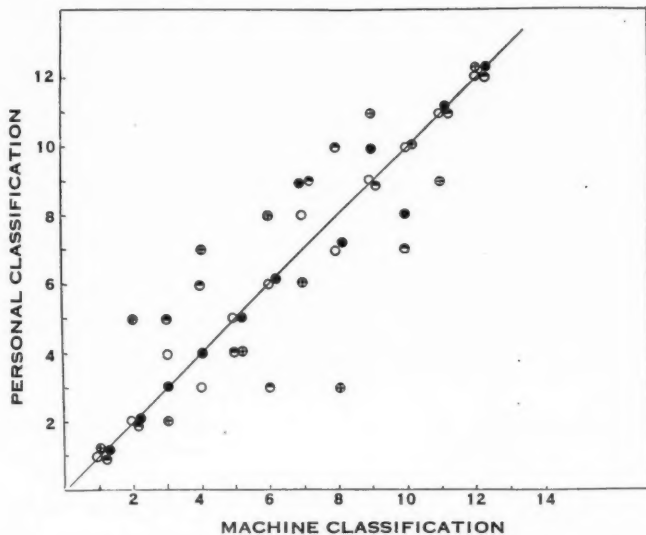


FIG. 7. Relation between hand evaluation and results of fibre-pulling apparatus, in the determination of relative fibre length in greases. The four symbols refer to four different observers.

Structure of Fibres in Soap-Oil Systems

Examination of soap-oil systems under the microscope, particularly by transmitted polarized light, shows a definite two-phase system consisting of a suspension of fibres in the oil. The larger fibre structures are seen to be made up of smaller units more or less parallelized to form a grosser unit larger in both length and cross-section. Further detailed examinations of such structures were carried out.

Orientation of Fibres

Lubricating greases are manufactured in general by heating a mixture of soap and oil to a definite temperature and then allowing the mixture to cool under agitation. Such agitation provides some means for an orientation of extremely fine fibrils to grosser structures. Any method of examination entailing a directional force, e.g., the pulling out of a string or fibre by hand, will obviously serve also to parallelize or orientate a number of fibrils to a larger fibre. Even the preparation of a microscope slide with the necessary removal of a sample from a container to the slide will bring about some appreciable orientation.

This ease of orientation to larger structures was easily shown by experiment. A sample of a sodium base grease was carefully transferred to a microscope slide. Only minor local parallelized areas were observed between crossed Nicols. The tip of a fine glass rod was then carefully applied to the sample and drawn through it. Each stroke was observed to bring about an orientation of finer structures in the direction of the applied force so that gross fibres were produced. Fig. 6 shows a photomicrograph of a portion of this field taken by transmitted polarized light. Two of these gross fibres are clearly shown to consist of parallel bundles of finer fibres. It should be noted that some of the apparent discontinuities in the solid phase are due to the bending of the fibre in the direction of observation, throwing these portions out of focus.

A similar experiment was carried out to show orientation of these fibres during flow. A sample of sodium soap grease of medium fibre texture was made to flow through a capillary by air pressure. A portion of the capillary filled with grease was then cut off, and examined between crossed Nicols. An excellent degree of orientation of the soap fibres in the direction of stress was observed.

These systems show a structural viscosity during flow, i.e., the flow-pressure curve is convex to the pressure axis. Orientation of the dispersed phase must result in a decrease in internal friction, and the degree of orientation increases with the stress. It would appear therefore that orientation is a major factor in the reduction of viscosity at increased pressures, leading to linear flow according to Poiseuille's law when mutual interference among particles of the dispersed phase has been removed by streamlining.

Investigation by Means of the Micro-manipulator

Further interesting information was obtained on the composition and properties of these fibres by the use of a micro-manipulator. This instrument consists essentially of three mounted tubes in which are held long glass rods terminating in very fine needles. One of the needles is on one side and two are on the other side; the three can be made to meet in the centre under the view of a microscope. Each needle is separately movable in nearly all directions by separate fine adjustment screws for each motion. One of the paired needles has a right-angled turn near the point and it can therefore be used in conjunction with the other needle on its side for holding an object of microscopic dimensions. The single needle opposite can be used for a tearing, pulling or bending action on the specimen. In the present work, a small sample of the soap-oil dispersion was placed directly on the needles for examination. In most instances, the magnification used was 60 to 200 diameters in order to preserve a relatively larger field for study.

When a pulling stress was exerted on the samples of dispersions under test, various effects were observed, depending on the composition and properties of the soap dispersion. In some instances, long fibres could be drawn out from the sample. With other materials, this "string-out" was virtually nil, since breakage occurred prior to the production of any appreciable amount of distortion. Table II shows the constitution of eleven commercial lubricating greases, in relation to the property of string-out.

TABLE II
FIBRE-FORMING PROPERTIES OF LUBRICATING GREASES

—	Grease No.	Type	Soap stock	Oil
A. Non-fibre-forming	1	Ca	Mixed fats*	150 vis. at 100° F.; 70 V.I.
	2	Ca	Mixed fatty acids	300 vis. at 100° F.; 70 V.I.
	3	Ca	Mixed fats and mixed fatty acids	900 vis. at 100° F.; 40 V.I.
	4	Na	Stearic acid	330 vis. at 100° F.; 40 V.I.
	5	Na	Stearic acid	190 vis. at 210° F.; 80 V.I.
	6	Al	Stearic acid	115 vis. at 210° F.; 40 V.I.
B. Fibre-forming	7	Na	Mixed fats	190 vis. at 210° F.; 80 V.I.
	8	Na	Mixed fats	300 vis. at 100° F.; 70 V.I.
	9	Na	Mixed fats	50 : 50 proportion 150 vis. at 100° F.; 70 V.I. and 190 vis. at 210° F.; 80 V.I.
	10	Na	Mutton tallow	330 vis. at 100° F.; 40 V.I.
	11	Na	Mixed fats	190 vis. at 210° F.; 80 V.I. (with some 150 vis. at 100° F.; 70 V.I.)

* Mixture of fleshings and lard stearin.

A sharp distinction in fibre-forming capacity is noted between these two groups. The property of stringing out under stress is obtained only with the sodium base greases that had been manufactured from fats. The presence of glycerol in the dispersion is therefore necessary for the appearance of this property.

In order to observe the effect of a shearing force on a dispersion containing relatively coarsely dispersed fibrils of more discrete nature, dispersions were prepared of various materials in oil, including fibres of rayon, milkweed, and sulphite pulp. Such systems show remarkable similarity in physical properties to ordinary lubricating greases. A typical example is a very fine rayon cut up into very short lengths and incorporated into an S.A.E. 60 oil to form a grease. The examination of this system by stressing in the micro-manipulator showed very striking results. Long fibres could be readily pulled out from the sample. The individual pieces of fibre were orientated during the pull, overlapping along their length to form a coherent larger unit. It was further clearly observed that the drawing out of this "macro-fibre" was undoubtedly a result of the sliding of the individual fibres over one another in an extension of the overlapping arrangement. The orientation of the soap fibres in an oil dispersion under a shearing force, discussed in a previous section, is undoubtedly an instance of the same phenomenon.

During these experiments on fibre formation with the micro-manipulator, it was noted that in some instances, the fibre formed by pulling snapped back into the remainder of the samples after breaking. A high degree of elasticity appeared to be involved. In other systems, the fibre appeared rather more plastic than elastic. Examination of fibre bundles in a sample of the grease on a microscope slide, by distortion with a very fine glass rod, indicated, however, only flexibility and no evidence of elasticity. In the systems that appeared elastic with the micro-manipulator, "bead-like" structures were noted along the newly formed fibre. These bodies could be made to move along the fibre, retaining their spherical form, and were found to be not visible between crossed Nicols. These structures are undoubtedly oil globules. It would appear that this oil is squeezed out during the pulling out of the fibre, and the apparent elasticity of the newly formed fibre is probably due to the surface tension of the oil seeking to reduce its surface to a minimum. The same phenomenon was observed in the non-soap systems containing rayon, milkweed, or sulphite cellulose fibres in oil suspension. It is apparent therefore that a group of fibres may be elastic owing to the surface tension of the liquid medium surrounding the fibres, whereas the individual fibres themselves are essentially inelastic, i.e., in the sense of "high-stretch elasticity" rather than obedience to Hooke's law. Flexibility, as contrasted with elasticity, is easily attained in a system of this kind as a result of the freedom of motion of the orientated fibrils with respect to one another.

Discussion

The commoner forms of lubricating greases are two-phase systems, consisting of a dispersion of soap particles in mineral oil. The texture and other physical properties, and hence also the industrial application of these materials, depends to a large extent on the degree of dispersion of the soap. It is therefore of particular interest to attempt to evaluate the various factors governing this degree of dispersion and the properties of the units of the dispersed phase:

The texture of calcium base greases and of ordinary aluminium base greases, without special additives, is always very short and buttery. Microscopic examination shows that the degree of dispersion of these soaps is very high, and any fibres present are extremely short. In sodium soap greases, however, a great range of fibre dimensions is readily obtainable. The texture varies correspondingly, from a smooth unctuous feel and appearance with very short fibres, to a rough, ropy appearance and feel with long heavy soap fibres in suspension.

In the manufacture of a sodium soap grease, the mixture of soap and oil (or fatty substance, alkali, and oil) is heated to an elevated temperature and the mixture is then allowed to cool. It has been shown previously by the writers (3) that sodium soaps show the phenomenon of partial melting in stages, and it is apparent that in the manufacture of a grease this melting must proceed to a sufficiently advanced stage to allow recrystallization to proceed. The amount of shear used also plays a part since the partially melted soap is still relatively unaffected by a non-polar mineral oil in the absence of glycerol. The soap is not wet by the oil under these conditions, under the influence of ordinary shearing forces through the use of double-action agitators, or when further elevated temperatures are used to disperse the soap. On cooling, very short fibres are obtained. The texture of such systems is short and buttery.

The writers have previously shown, however, that in the presence of glycerol the soap is dispersed at a relatively low temperature (4) and that the mineral oil is capable of wetting the soap (7). This is further well demonstrated also in considerations of surface tension in such systems (5). The recrystallization of the soap in such systems, containing glycerol, brings about the production of long fibres. The length is then dependent on the amount of glycerol available, the viscosity and polarity of the oil used, the soap concentration, rate of cooling of the dispersion and other factors.

The present work shows what variations may be obtained in fibre lengths under different conditions.

The relatively gross fibres that can be pulled out by hand from a finished grease are obviously not formed directly as a result of recrystallization. It has been amply shown in the course of this work that the effect of a shearing force is to bring about a parallelization of fibres in the grease system. The very act of pulling out a fibre by hand as commonly practised in the industry in a qualitative evaluation of a grease, actually brings about the formation

of a large "fibre" which obviously consists of a number of pre-existing fibres orientated and overlapping along their length. It is apparent that the length of this gross fibre that can be drawn from a grease is dependent on the length of the pre-existing fibre in the grease, since the overlapping of short fibres would lead to a relatively short break, and increase in length of these components would lead to longer gross fibre bundles.

The fibres that are present in the grease prior to any such pull-out are also not directly resultant from recrystallization. Grease manufacture always involves agitation during cooling, and it is apparent that this constitutes also a shearing force that has an orientating effect on pre-existing fibre forms. The effect of this shear will be discussed more fully elsewhere (6), but it may be stated that the amount of shear used is an important factor. There is involved during the cooling of the soap-oil mixture then, an orientation of smaller fibrils to larger fibre bundles. The extent to which fibres can be built up at this stage will depend also on the length of the pre-existing fibrils, owing to the variation in coherence of the parallelized bundles with length of components.

The dimensions of the crystallites formed by recrystallization of the soap are very probably dependent on the presence of glycerol (or similar additive), which exerts a solvent action on the soap and then enables the oil to wet the soap crystals, allowing for the building up of larger crystallites or fine fibrils by collisions. It has been shown by Marton, McBain, and Vold (8), that extremely fine fibres or ribbons of sodium laurate are produced by drying aqueous solutions of the soap on a fine screen. Electron microscope photographs show that the finest fibres actually approach molecular dimensions. The length of these fibres is comparatively very great. Such ribbon-like crystallites of ultimate dimensions in cross-section are very probably the starting point in recrystallization.

The presence of glycerol with its attendant effect in bringing about a wetting of the soap by the mineral oil, undoubtedly leads to a facilitation of the growth of these newly formed crystallites. This will then be reflected in later stages in the formation of larger fibrils, fibres, and gross fibres, because of the orientation effects and overlapping of fibres discussed above.

It should be noted that this discussion on fibre formation applies in the first instance to sodium soap greases. Special factors enter into a consideration of calcium and aluminium soap greases, and these will be discussed separately in forthcoming publications.

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LOW TEMPERATURE SAPONIFICATION IN ANHYDROUS SYSTEMS¹

BY WILFRED GALLAY² AND IRA E. PUDDINGTON²

Abstract

Finely dispersed sodium hydroxide, suspended in mineral oil, was used to saponify fatty acids and fats in mineral oil solution. Saponification was carried rapidly to completion at 60° C. The properties of the resultant soap suspensions in oil are discussed. The degree of saturation of the fatty acids or fats is of importance in the viscosity of the suspension formed. Low molecular weight fatty acids down to acetic were also saponified by this method. Of various fats used, only mutton tallow was completely saponified at low temperature.

Finely dispersed calcium hydroxide in mineral oil suspension effects complete saponification of fatty acids in mineral oil solution at a temperature of 50° C. and of mutton tallow at a somewhat higher temperature. The effect of degree of unsaturation, and the use of other fats are discussed. Small quantities of added water are shown to promote saponification.

This saponification procedure was used also to prepare suspensions in oil of the following metal soaps: aluminium, magnesium, barium, lead, lithium. Some properties of the suspensions are described.

Part I—Sodium Soaps

INTRODUCTION

Sodium soaps are manufactured by the reaction of a fatty material with an aqueous solution of alkali, either in batch form or in a continuous system. The batch method is still commonly practised, in which the fatty material and aqueous alkali solution are heated under agitation in a large vessel, following which the soap is salted out, and the glycerol is recovered from the liquor. The less common continuous method involves the reaction of the fatty material with a concentrated aqueous alkali solution in a coil reaction tube at high temperatures, e.g., over 400° F. The raw materials are metered into the system and the resultant soap and liquor are sprayed into a vacuum chamber, in which the glycerol and water are flashed off. The disadvantages of water in this reaction are obvious, e.g., in the extra heat consumed, and in the cost of glycerol recovery.

Saponification in an aqueous medium is generally considered to be a heterogeneous reaction, the rate depending to a large degree on the extent of the interfacial surface developed between fatty material and aqueous solution. Smith (8) has obtained data from which he concludes that the reaction is of the homogeneous type, since his reaction rates in this autocatalytic reaction appear unexplainable on the basis of developed interfacial surface area. His

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concept of a homogeneous reaction in this saponification involves a bipolar ionic micelle of soap, which acts as a solvent for both alkali and fatty material. The reaction is thus autocatalytic with the continuous formation of additional quantities of soap.

The work of Kokatnur (5) is of particular interest in this connection. This development involves anhydrous saponification in a non-aqueous medium. Anhydrous powdered sodium hydroxide is reacted with a solution of the fatty material in kerosene at a temperature of 200 to 215° C. in order to effect saponification, and the mixture of glycerol and kerosene is removed by distillation. This procedure has been carried out also by Jacobs (4), who notes further that the rate of reaction is greatly increased by the use of a special form of alkali, manufactured by the dehydration of a sodium hydroxide solution in the presence of kerosene (7). The higher reactivity of this form of caustic soda is ascribed to a greater surface area, since flat platelets are obtained as a result of this crystallization procedure.

It is noted that a heterogeneous reaction is assumed in the above work, and it is in fact difficult to avoid this conception where the alkali is in a relatively gross state of subdivision.

The present work forms a part of an extensive investigation on the subject of lubricating greases. In the present industrial procedure for the manufacture of sodium soap greases, the soap is made from alkali and fat or fatty acids or both, in an aqueous medium. The resultant soap is then dispersed in a mineral oil at a high temperature as a separate operation in order to form the desired grease. The water is removed as desired by suitable temperature control either prior to, or during, the addition of the mineral oil. A method of saponification *in situ* in the oil medium would have the important advantages, among others, of carrying out the manufacture in one step, and the obviation of the addition and removal of water.

The procedure of Kokatnur described above involves the use of a high temperature to attain this end. The saponification experiments described below were carried out at a relatively low temperature in anhydrous systems using a readily prepared very finely dispersed sodium hydroxide, in mineral oil medium.

ANHYDROUS SAPONIFICATION BY MEANS OF RELATIVELY COARSELY DISPERSED ALKALI

Fatty Acids

A number of preliminary experiments were carried out using ordinary flake sodium hydroxide. The addition of flake caustic to a solution of a fatty acid in a mineral oil brought about virtually no heat of reaction, and it was apparent that the amount of saponification produced was negligible. Suspensions of flake caustic in a mineral oil solution of a fatty acid were then passed through a colloid mill, and a partial saponification was effected, but the resultant mixture contained large proportions of free fatty acid and free alkali.

Considerably better results were obtained when the flake caustic was first ground in a hand-operated disk mill and then reacted with the fatty acid solution in a colloid mill as described above. The degree of saponification was however still unsatisfactorily low.

Preheating the suspension of powdered caustic in the fatty acid solution to a temperature of about 135 to 140° C. effected a considerably increased degree of reaction. Some saponification took place during this preheating as evidenced by the increase in viscosity of the suspension. The particles of alkali, however, became coated with the soap formed and further reaction was very slow or completely inhibited. The passage of the preheated suspension through the colloid mill was then shown to assist greatly in exposing fresh surfaces of alkali, and a fairly good degree of saponification was obtained.

This powdered sodium hydroxide was suspended in the solution of the fatty acid in the mineral oil and the suspension was heated to about 135° C. The suspension was passed through the colloid mill and then a sample of the material was thoroughly extracted in a Soxhlet with petroleic ether, and the extract evaporated to constant weight. Determination of the saponification number was then carried out according to the standard procedure. The following examples illustrate the type of results obtained.

1. Sodium hydroxide (3.5 gm.), stearic acid (20 gm.), and 450 vis. 70 V.I. oil (300 gm.) preheated to 135° C., after one passage through the colloid mill, showed 90% saponification.
2. The same mixture preheated also to 135° C., after two passages through the colloid mill, showed 95% saponification.
3. Sodium hydroxide (3.2 gm.), stearic acid (20 gm.), and 190 vis. (at 210° F.) 80 V.I. oil (200 gm.), preheated to 100° C., and passed through the colloid mill once, showed 83% saponification.

Fats

Using fatty acids, it was noted that simple heating of the alkali and fatty acid solution brought about a small degree of saponification. With fats, there was no noticeable rise in viscosity of the mixture. It is apparent that the ease of saponification is reduced. The combined effect of preheating the suspension and shearing in the colloid mill is shown by the following examples.

1. Sodium hydroxide (4.2 gm.), mutton tallow (20 gm.), and 300 vis. 70 V.I. oil (300 gm.), preheated to 135° C., after one passage through the colloid mill, showed 85% saponification.
2. The same mixture, preheated also to 135° C., after two passages through the colloid mill showed 90% saponification.
3. Sodium hydroxide (4.2 gm.), mutton tallow (20 gm.), and 190 vis. (at 210° F.) 80 V.I. oil (200 gm.), preheated to 100° C., after one passage through the colloid mill, showed 67% saponification.
4. The same mixture, preheated also to 100° C., after two passages through the colloid mill, showed 83% saponification.

5. Sodium hydroxide (4.2 gm.), mutton tallow (20 gm.), and 450 vis. 70 V.I. oil (200 gm.), preheated to 150° C. for 15 min. then cooled to 60° C. and passed once through the colloid mill, showed 83% saponification.

The reaction between solid alkali and fatty matter in mineral oil solution must necessarily be a heterogeneous one initially. When a certain amount of soap has been formed, then a homogeneous reaction in the soap phase may take place. The solvent action of the soap for the reacting mixture is greatly increased with rise in temperature, probably particularly after the bidimensional melting point has been attained (1). The effect of high shear may therefore be twofold, viz. (1) a further comminution of the alkali particles, (2) a removal of the soap from the surface of the alkali, allowing for a further surface reaction, with possibly a subsequent autocatalysis as a result of further soap formation. The viscosity of the oil used will undoubtedly have an effect, since a greater amount of shear will be provided by a more viscous oil.

In general, it is noted that the results obtained above are far from satisfactory in the preparation of neutral soaps.

ANHYDROUS SAPONIFICATION BY MEANS OF FINELY DISPERSED ALKALI

Preparation of Finely Dispersed Sodium Hydroxide

Dispersion of the sodium hydroxide in order to provide a greatly extended specific surface appeared to have promise in promoting increased reactivity. Suspensions of sodium hydroxide in 30 to 35% concentration in mineral oils were prepared by simple mixing, and these suspensions were then passed through the colloid mill. Microscopic observation showed that the sodium hydroxide was dispersed in the form of rods. The system was polydisperse, with most of the rods less than 5 μ in length, and a small fraction approaching the limit of resolution of the microscope. Fig. 1 shows a photomicrograph of such a finely divided suspension of sodium hydroxide in a mineral oil.

The suspension showed settling on standing for several days, but there was essentially no agglomeration since the system was readily redispersed by gentle shaking. The addition of 0.5% sodium stearate to the suspension had an important suspending action in preventing settling. The viscosity index or polarity of the oil used had little effect on the properties of the suspension. Oils of higher viscosity yielded somewhat more finely divided suspensions, probably as a result of the greater shearing action in the mill.

The effect of ball-milling was then investigated. Sodium hydroxide suspensions (35% concentration) were ground in a 2 quart ball-mill with quartz pebbles. Initial experiments were carried out over 18 hr., but it was then found that this time could be greatly reduced. The degree of dispersion attained was essentially the same as that following shearing in the colloid mill. Comparative saponification experiments using the suspensions formed by these two procedures showed also essentially the same degree of reactivity.

The stability of these suspensions with regard to reactivity in saponification was very good. The reactivity of a suspension after one year of standing in the laboratory was found to be satisfactory.

SAPONIFICATION

A. Fatty Acids

The finely dispersed sodium hydroxide in mineral oil was found to react with a solution of stearic acid in a mineral oil at a low temperature, e.g. 60° C., and the saponification went rapidly to completion. The difference in reactivity between the finely and coarsely dispersed alkali is very great. The concentration of fatty acid used has also a minor effect in the initial temperature required.

The physical properties of the resultant soap dispersions in oil depend markedly on the degree of unsaturation of the fatty acid used. This is shown in the following examples.

1. Stearic Acid

The fatty acid was dissolved in the mineral oil at 50° C., and the calculated amount of sodium hydroxide dispersion in oil added. The mixture was heated with agitation to about 60° C., or somewhat higher, the actual temperature depending on the fatty acid concentration. A sudden increase in viscosity was observed and the reaction went to completion in a short time. A polar oil, e.g. 500 vis. 40 V.I., yielded a soap-oil suspension or grease which was smooth and very short in texture. The suspension was stable, i.e., no bleeding of oil was observed on standing.

Microscopic observation showed that the sodium stearate produced by this *in situ* method was dispersed in the form of very short rod-shaped fibres, which were remarkably uniform in dimensions. No agglomeration of these discrete rods was observed either initially or on standing. It is apparent that the degree of dispersion will depend in part on the number of nuclei at the time of crystallization, and the protection against growth afforded by the medium. The high degree of dispersion results in a "high yield", i.e., a large viscosity relative to the concentration of the dispersed phase.

Fig. 2 shows a 10% sodium stearate dispersion in 500 vis. 40 V.I. oil, prepared by the anhydrous saponification method. Fig. 3 shows a similar dispersion in a 500 vis. 95 V.I. oil. It is noted that the degree of dispersion is somewhat less where a non-polar oil is used as the medium. Fig. 4 shows a photomicrograph of the same dispersion as used in Fig. 2, but prepared by a dry slide technique (3). The removal of the oil has resulted in a clumping of the formerly discrete rod-shaped fibres.

2. Oleic Acid

The fatty acid was dissolved in the mineral oil at room temperature, and the calculated amount of sodium hydroxide added. The mixture was heated with agitation to about 60° C. As in the case of stearic acid, a sudden increase in viscosity was observed, and the saponification went rapidly to completion. The resultant soap suspension had a very short texture and was stable with regard to bleeding of oil.

PLATE I

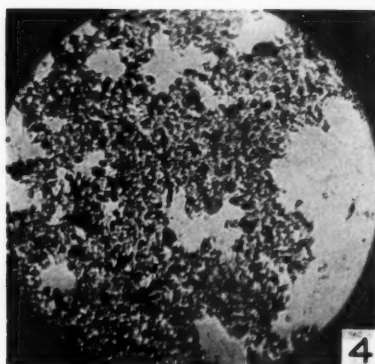
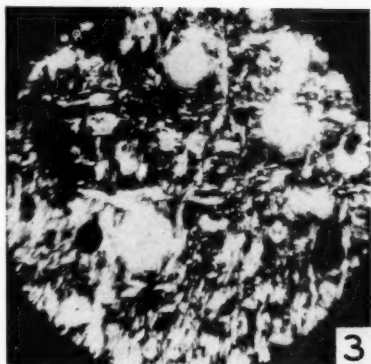
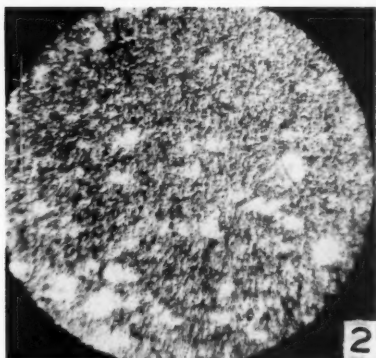
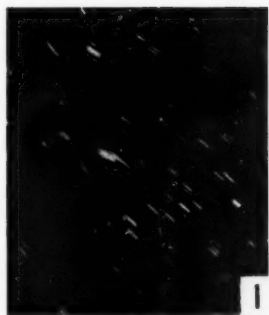


FIG. 1. Finely dispersed rod-shaped particles of sodium hydroxide in mineral oil suspension. Polarized light. $\times 80$. FIG. 2. A 10% dispersion of sodium stearate in 500 vis. 40 V.I. oil, prepared by anhydrous saponification. Polarized light. $\times 80$. FIG. 3. A 10% dispersion of sodium stearate in 500 vis. 95 V.I. oil, prepared by anhydrous saponification. Polarized light. $\times 80$. FIG. 4. A 10% dispersion of sodium stearate in 500 vis. 40 V.I. oil, prepared by anhydrous saponification. Dry slide technique. Polarized light. $\times 80$.

PLATE II

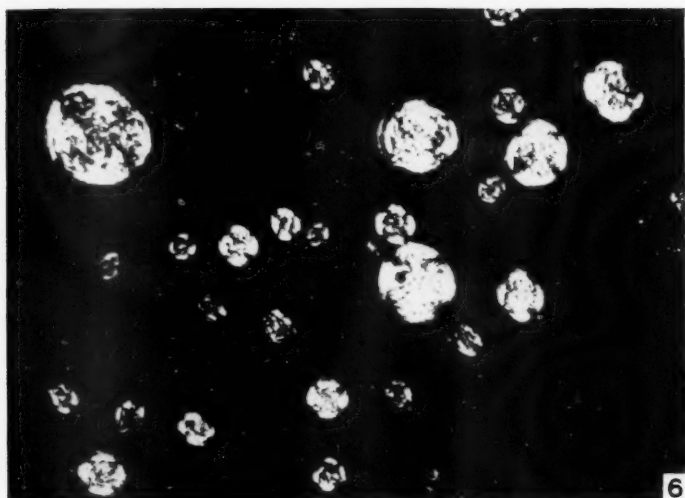
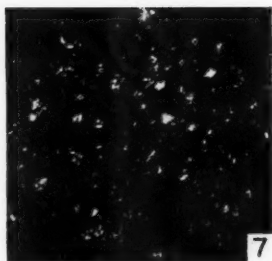
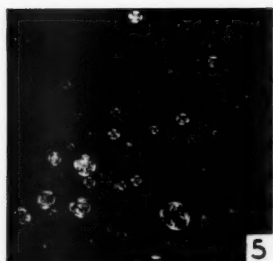


FIG. 5. A 10% dispersion of sodium oleate in 500 vis. 40 V.I. oil, prepared by anhydrous saponification. Polarized light. $\times 60$. FIG. 6. Same dispersion as in Fig. 5. Polarized light. $\times 205$. FIG. 7. A 10% dispersion of mutton tallow soaps in 500 vis. 40 V.I. oil, prepared by anhydrous saponification. Polarized light. $\times 60$.

The viscosity of the suspension was very low. Microscopic observation showed a remarkable difference from the sodium stearate suspension described in the preceding section. With sodium oleate, the small rod-shaped fibres were found to be agglomerated to spherical clusters. Virtually no discrete rods were present. The clusters appeared to have an outside shell of more densely packed particles, and a dark cross or hylum was observed in polarized light. It is apparent that the formation of clusters will result in a lower viscosity for a given concentration, owing to lack of dispersion.

Fig. 5 shows such a dispersion in 10% concentration in 500 vis. 40 V.I. oil. Fig. 6 shows a portion of the above sample under higher magnification, and one cluster is clearly shown.

3. *Mixed Fatty Acids*

Cottonseed fatty acids were dissolved in 450 vis. 70 V.I. mineral oil at 50° C. and the calculated quantity of sodium hydroxide dispersion in oil added. The mixture was heated with agitation to about 60° C. A sudden increase in viscosity was noted and the saponification proceeded rapidly to completion. The texture of the resultant soap-oil dispersion was short, and the yield obtained was intermediate between similar sodium stearate and sodium oleate dispersions.

Microscopic observation showed that a portion of the suspension was in the form of short discrete rod-like fibres identical with those formed by sodium stearate with this mode of preparation. Another portion of the suspension was in the form of agglomerated clusters of these fine fibres, similar to those shown by sodium oleate. It is apparent therefore that mixed fatty acids behave in additive fashion with respect to the saturated and unsaturated fatty acid components.

4. *Fatty Acids of Low Molecular Weight*

The use of aliphatic acids of low molecular weight showed interesting results. A solution of caproic acid in mineral oil reacted immediately with the sodium hydroxide suspension in mineral oil at room temperature, and the saponification went rapidly to completion. Similar results were obtained with butyric acid. These suspensions were short in texture and showed a high yield similar to stearic acid. The solubility of acetic acid in mineral oil at room temperature is very low. On heating to a temperature sufficiently high for solution of this acid, subsequent saponification with the alkali dispersion was very difficult owing to the high velocity of the reaction. Agitation by ordinary means was not possible. A 50 : 50 mixture of oleic or stearic acid with acetic acid was found to be soluble in mineral oil at room temperature. These mixtures were found to react readily with the sodium hydroxide dispersion at room temperature, and the saponification appeared to go to completion. The texture of the soap suspensions was rough, however, and some bleeding of oil took place on standing. It would appear that the oil-holding capacity of sodium acetate is relatively low.

B. Fats

Mutton tallow was dissolved in mineral oil at 50° C., and the calculated quantity of sodium hydroxide dispersion was added. On heating the mixture with agitation to a temperature of about 60° C., saponification proceeded rapidly to completion.

Suspensions of mutton tallow soaps were prepared in this way in 750 vis. 40 V.I. oil, 500 vis. 40 V.I. oil, 900 vis. 40 V.I. oil, and 500 vis. 95 V.I. oil. It was found, analogous to previous cases noted earlier, that a lower yield was obtained with an oil of higher V.I. As with the mixed fatty acids, the dispersed mutton tallow soaps in oil were in the form of both discrete rods and agglomerated clusters. Fig. 7 shows a photomicrograph of such a suspension in 500 vis. 40 V.I. oil.

Other fats such as cottonseed oil, fleshings, and lard stearin, and synthetic glyceryl tristearate were tried out in this anhydrous saponification reaction. However, the degree of saponification was much lower than with mutton tallow, under the low temperature condition.

On heating the mixtures of fat solutions and alkali dispersions to 80° C., the following results were obtained.

1. Synthetic glyceryl tristearate—no increase in viscosity.
 2. Stearin—very little increase in viscosity.
 3. Mixture of stearin and cottonseed oil, of the same iodine value as mutton tallow,—the yield was better than that with stearin alone, but very much lower than that with mutton tallow.
 4. Fleshings—appreciable increase in viscosity was observed at 65° C., but the yield was poor.
 5. Synthetic glyceryl oleate—poor yield, similar to that with oleic acid.
- It would appear that the structure of the fat is important from the point of view of ease of saponification in this reaction.

Degree of Saponification and Viscosity of Soap-Oil Suspensions Prepared by Anhydrous Saponification

Table I shows the results of an inspection† of a number of samples of soap-oil dispersions, prepared in the laboratory by the *in situ* anhydrous saponification method. The worked and unworked penetrations are the consistencies obtained by the standard A.S.T.M. Penetrometer method.

The viscosities obtained with the saturated fatty acid soaps are very greatly superior to those obtained industrially, using the common method of aqueous saponification followed by dispersion in oil. The yields with the unsaturated fatty acids are low as a result of the peculiar agglomeration effect previously noted. A subsequent paper will deal with the effect of high shear on these systems (2).

† Inspection carried out by Imperial Oil Ltd.

TABLE I
INSPECTION DATA ON SOAP-OIL DISPERSIONS

Fatty material	Mineral oil	% Soap	% Water	% Acidity	% Alkalinity	Penetration	
						Worked	Unworked
Stearic acid	190 vis. 80 V.I.	10	—	0.35	—	165	214
Stearic acid	500 vis. 40 V.I.	10	0.3	1.30	—	108	208
Stearic acid	500 vis. 95 V.I.	10	0.4	0.42	—	167	238
Stearic acid	330 vis. 40 V.I.	3	—	—	—	Too soft	
Stearic acid	500 vis. 40 V.I.	5	—	—	—	Too soft	
Cottonseed fatty acids*	450 vis. 70 V.I.	10	—	—	0.06	218	240
Mutton tallow*	190 vis. 80 V.I.	10	—	—	0.10	196	335
Mutton tallow*	500 vis. 95 V.I.	10	—	—	0.08	304	374
Mutton tallow*	750 vis. 70 V.I.	10	—	—	0.06	176	248
Mutton tallow	900 vis. 40 V.I.	10	—	—	0.22	194	305
Mutton tallow	500 vis. 40 V.I.	20	—	—	0.50	88	213

* These soap suspensions were passed once through a colloid mill, subsequent to saponification.

Part II—Calcium Soaps

INTRODUCTION

Calcium soaps are generally prepared by the interaction between a soluble calcium salt and the corresponding sodium soap, both in aqueous solution. The precipitated calcium soap is purified by washing and is dried and ground for further use. Jacobs (4) has described the direct manufacture of calcium soap from calcium hydroxide and tallow in a kerosene medium at high temperatures. The method is similar to that which he used in the preparation of sodium soap, and the temperature necessary is stated to be within the range of the kerosene method (end b.p. 310° C.).

In the manufacture of sett greases, calcium hydroxide is saponified directly with a solution of rosin acids in mineral oil at low temperatures. Naphthenic acids are readily saponified by this method. McKee (6) has described the saponification of oleic acid with calcium hydroxide in an oil medium, using temperatures of 93 to 115° C. In general, the present industrially used procedure for the manufacture of calcium soap greases involves two steps. The fatty material is saponified with calcium hydroxide in aqueous medium at high temperatures under pressure. The resultant soap is then dispersed in oil to form a suspension of the desired characteristics.

The present work describes the saponification of fatty materials with calcium hydroxide at low temperatures, e.g., 50° C., in a mineral oil medium to form soap-oil suspensions directly. The method has obvious advantages in eliminating the addition and removal of water, and the products possess certain desirable features in texture and stability.

Preliminary Experiments

Suspensions of calcium hydroxide, taken from partially used laboratory reagent stores, were prepared in various mineral oils. These suspensions

were then mixed with solutions of fatty acid or fat in mineral oil. No reaction was observed at low temperatures. On heating the mixtures to about 140° C., a partial saponification was obtained as evidenced by a noticeable increase in viscosity. Somewhat improved results were obtained when a calcium hydroxide suspension, which had been passed through a colloid mill prior to mixing with the fat solution, was used. After cooling the suspensions, it was noted that the degree of saponification continued to increase on standing. No noticeable increase in reaction was obtained through the use of accelerators of the Twitchell type or triethanolamine. Small quantities of finely dispersed sodium hydroxide were not effective in promoting an increased degree of saponification. It was noted that rapid cooling of the soap suspension resulted in a very finely dispersed suspension; in some cases no resolution could be obtained at high magnifications. In the same system, slow cooling resulted in relatively large crystals.

FORMATION OF CALCIUM SOAPS IN ESSENTIALLY ANHYDROUS SYSTEMS

1. *Fatty Acids*

After further trials, it was found that slaked lime containing a slight excess of water showed excellent activity in saponification of fatty acids at low temperatures. The calcium hydroxide suspension was prepared as follows. Water (50 gm.) was added to powdered calcium oxide (112 gm.; 100 mesh). Allowing for the loss of water during the reaction, and assuming complete slaking, there was obtained a calcium hydroxide containing 4.5% water. This powder was then mixed with mineral oil to form a suspension of 15% concentration, and the suspension was passed twice through a hand operated homogenizer. The finely divided alkali dispersion was then reacted with a solution of fatty acid in mineral oil.

At about 50° C., the saponification with stearic acid went rapidly to completion. Considerable heat was evolved, and care had to be taken to avoid a reaction rate so rapid that insufficient time was available for proper mixing. The resultant soap suspension was smooth in texture and stable with regard to oil-holding capacity. The soap concentration may be varied within wide limits.

The concentration of water in the suspension is an important factor in the properties of the material. Calcium soap greases are in general unstable in anhydrous oil suspension, unless special additives are used. The effect of the water in these systems is complex and will be dealt with elsewhere (2). The concentration of water used in this *in situ* saponification may be varied within wide limits, and microscopic observation shows that the water is very finely dispersed.

Activity of Calcium Hydroxide with Time

The possibility of the deterioration with time of the calcium hydroxide, as such or in oil suspension, is obviously of importance. A recrystallization with consequent reduction of specific surface would lead to a decreased activity of the material. Samples of calcium hydroxide in oil suspension were with-

drawn from one batch over a period of months, and no decrease in activity of the alkali was observed. The heat evolved during saponification served as a measure of this activity.

For the determination of the stability of the calcium hydroxide in powdered form, the following experiments were carried out. A quantity of the slaked lime was prepared as shown above. After various intervals of storage in a glass bottle fitted with a screw cap, the alkali was used as follows. The alkali (15 gm.) was added to 500 vis. 40 V.I. oil (85 gm.), and the mixture was passed twice through a hand operated homogenizer. A portion (10 gm.) of this suspension preheated to 50° C. was then added to a solution containing 12 gm. of stearic acid in 75 gm. of 500 vis. 40 V.I. oil also at 50° C. The mixture was stirred mechanically for 30 sec. and the final temperature was then read at the centre of the mixture. This procedure was repeated at stated intervals, using a freshly prepared alkali-oil slurry in each experiment, the slurry being prepared from the same lot of calcium hydroxide. Table II shows the activity in terms of increase in temperature observed during the reaction.

TABLE II
ACTIVITY OF CALCIUM HYDROXIDE WITH TIME

Age of alkali, days	Increase in temp., ° C.
0	9
1	8
5	10
11	10
18	10
26	9
35	10

It is apparent that the reactivity of the calcium hydroxide is well maintained over this time interval. Trials with other samples of calcium hydroxide known to have been stored for some time showed similar results. Eighteen months' storage in one experiment lead to a decrease in reactivity corresponding to 1.7° C. It is obvious, however, that any large degree of carbonation must be avoided.

Effect of Water

Previous saponification trials included small quantities of water, since these are necessary to provide stability in the resultant suspension. The effect of water was also determined as a separate factor as shown in the following examples.

A sample of calcium hydroxide of commercial grade, taken from a large quantity in storage, was found to contain 0.5% of water by the Dean and Stark toluene distillation method. A suspension of the alkali in mineral oil was prepared, and allowed to react with a solution of stearic acid in mineral oil. At 45° C., an induction period of 5 min. was observed, following which a

maximum heat rise of 7° C. was noted during saponification. When saponification was carried out at 80° C., the reaction proceeded more rapidly, but the viscosity of the resultant soap suspension was relatively low. At 75° C., there was obtained also a very short induction period of reaction and a low consistency. After the addition of 1% of water to the calcium hydroxide suspension in oil, the subsequent induction period was considerably shortened to 45° C., and a greater heat rise was observed. The viscosity of the resultant soap suspension was also greatly improved.

Using a sample of calcium hydroxide of unknown history, a 10 to 12 min. induction period was noted prior to saponification at 45° C. and the temperature rise during the reaction was only 5° C. After the addition of 1% of water to the calcium hydroxide suspension in oil, the induction period was virtually nil. The maximum heat rise in the mixture was now 8° C., and the viscosity of the soap suspension was correspondingly greatly improved.

Effect of Initial Temperature

In view of variations observed in the viscosity of the soap-oil dispersion, depending on the temperature at which saponification was carried out, a number of trials were made at different initial temperatures. The calcium hydroxide dispersion and the stearic acid solution in oil were separately heated to the initial temperature noted. The two components were then mixed with mechanical agitation and the heat rise in the standard vessel was noted. A total volume of 100 cc. in a 150 cc. beaker was used.

TABLE III
EFFECT OF INITIAL TEMPERATURE ON SAPONIFICATION

Mixing temp., ° C.	Temp. rise, ° C.
39	16
40	17
48	16
73	15
84	17

It is noted that the heat rise is not appreciably affected by variations in reaction temperature. The yield obtained, i.e., the viscosity of the resultant soap suspension per unit concentration, decreased, however, in the order shown above. In order to obtain a good yield, it is necessary to use a relatively low reaction temperature, followed if necessary by the application of more heat. It is probable that the speed of the reaction, and consequent difficulty in stirring, is a factor in this matter.

Various Fatty Acids

The yield obtained on the saponification of unsaturated fatty acids is much lower than that with saturated fatty acids. This is similar to the results noted with sodium hydroxide in Part I. Cottonseed fatty acids yield intermediate results.

Saponification experiments were carried out on the following pure fatty acids: lauric, myristic, palmitic, and stearic. Of these, lauric and stearic acids showed good yields, palmitic acid a somewhat lesser yield, and myristic acid a relatively low yield.

The results obtained with caproic, butyric, and acetic acids were similar to those obtained in sodium soap formation. Acetic acid was used in conjunction with oleic acid to effect solubility in mineral oil at low temperatures.

2. *Fats*

Mutton tallow was shown to be quite readily saponifiable with calcium hydroxide by this method. As in saponification with caustic alkali, other fats were found to react much more slowly. Lard, stearin, cottonseed oil, and synthetic glyceryl tristearate showed no reaction at a temperature of 50° C., and even after heating to 95° C., only a partial saponification was reached. The yield obtained with mutton tallow is relatively low, owing probably to the large proportion of unsaturated fatty acids contained. Calcium soaps do not form long fibres (3) on crystallization in oil, and therefore the distinction of agglomeration of the unsaturated soap particles was not noted for calcium soaps.

Part III—Other Soaps

INTRODUCTION

Metallic soaps in general are prepared by the interaction of a soluble salt and the corresponding monovalent soap in aqueous solution. Several of the metallic soaps show ready dispersion in mineral oils and the resultant suspensions have in some cases desirable physical properties. The application of the anhydrous saponification method, described above, to the preparation of oil dispersions of these soaps is therefore of interest. There are given below brief summaries of the preparations and outstanding properties of these suspensions for several metals.

Aluminium Soaps

Aluminium metal and aluminium hydroxide were found to show no reaction with stearic acid, even after heating the mixture to 150° C., and passage through a colloid mill. Gelatinous aluminium hydroxide was prepared by precipitation with ammonium hydroxide and washing with water. The resultant gelatinous hydroxide was suspended in 500 vis. 40 V.I. oil by passage through a colloid mill. On addition of this slurry to a solution of stearic acid in oil, a partial saponification was obtained. It is noted that a large quantity of water must be removed by heating. Basic aluminium acetate was suspended in a mineral oil by passage through a colloid mill, and some saponification was obtained on reacting this suspension with stearic acid solution in oil. It was apparent from the odour of acetic that a portion of the acetic acid was replaced by stearic acid.

Aluminium powder and turnings were activated by shaking with a dilute solution of mercuric chloride in methyl alcohol. The sensitized aluminium

was added to a solution of stearic acid in oil, and saponification resulted after heating to 130° C.

The aluminium soap greases possess outstanding water resistance and stability. The texture may be varied widely with different formulations.

Magnesium Soaps

Lightly calcined magnesia was slaked to magnesium hydroxide with excess water. After standing overnight, the hydroxide was dried at 115° C., and suspended in 500 vis. 40 V.I. oil by passing through a colloid mill. Saponification was then carried out at a low temperature on mixing the suspension with a solution of the fatty material in oil. Other materials such as brucite or calcined magnesitic dolomite were found suitable for this reaction.

Stearic acid and cottonseed fatty acids yielded soap suspensions in excellent yields. Mutton tallow gave a much lower consistency. The magnesium soap greases have a relatively low melting point and are quite sensitive to excess alkali and speed of cooling. They are, however, stable on melting and resolidification, and possess a high degree of resistance to water.

Barium Soaps

Both hydrated barium hydroxide ($8\text{H}_2\text{O}$) and anhydrous barium hydroxide, after suspension in oil by means of the colloid mill, were found to react readily with an oil solution of a fatty acid. The yields were very good when the content of free fatty acid was properly adjusted. Water must be removed in the case of the hydrate.

The barium soap greases are stable to melting and resolidification, and show less sensitivity than the magnesium soap greases to small quantities of acids and alkalis. These suspensions show a relatively high melting point.

Lead Soaps

Commercial litharge was suspended in 900 vis. 40 V.I. oil by means of the colloid mill, and this suspension was then reacted at a low temperature with solutions of fatty acids in oil. The saponification proceeded rapidly to completion.

Unsaturated lead soaps are apparently soluble in mineral oils and the consistency of the solutions is very low. The suspensions of the saturated lead soaps show a low melting point, but are stable to melting and resolidification.

Lithium Soaps

Lithium hydroxide was suspended in mineral oil by passage through a colloid mill, and this suspension was found to saponify readily a solution of fatty acid in oil. The yields obtained were extraordinarily high.

Lithium stearate greases possess a high melting point and good water resistance. They are therefore of particular interest in that they combine the best qualities of sodium and calcium soap greases, without the major disadvantages.

Other Soaps

It was shown in test-tube experiments that the oxides or hydroxides of nickel, cobalt and manganese, in suspension in oil, were capable of saponifying stearic acid in oil solution.

INSPECTION DATA ON OILS USED*

Data	40 V.I. oils				70 V.I. oils		95 V.I. oil	80 V.I. oil
	300 vis.	500 vis.	750 vis.	900 vis.	300 vis.	450 vis.	500 vis.	190 vis.
Gravity, A.P.I.	24.1	23.2	—	22.6	28.9	—	29.1	22.0
Flash, ° F.	405	400	—	455	395	—	455	585
Vis. at 100° F., S.U.S.	333	498.0	742	929.1	309.1	472.2	471.7	531.1
Vis. at 210° F., S.U.S.	49.7	55.8	63.6	68.3	50.7	57.3	61.8	206.2
V.I.	49	47	41	34	76	69	96	79
Robinson Colour	10½	9½	—	9½	16½	—	12	—
Neutralization No.	0.26	0.50	0.44	0.28	0.02	0.048	0.028	0.04
Pour, ° F.	-30	-15	—	-10	-25	—	-20	+45

* Inspection carried out by Imperial Oil Ltd.

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THE RECRYSTALLIZATION OF SODIUM SOAPS IN MINERAL OILS¹

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Abstract

The effect of the following factors on the recrystallization of sodium soaps in mineral oils is described: rate of cooling, acidity and alkalinity of the soap, concentration of the soap, unsaturation in the soap, polarity of the oil, effect of a number of additives such as glycerol, and external shearing forces.

Non-polar mineral oil acts as an inert diluent and recrystallization is essentially that from a hot melt. The presence of polar compounds results in some solvent action on soap in the mesomorphic states, and the effect of shear on the form of the recrystallized soap in such systems is important.

The preparation of a sodium soap lubricating grease is essentially a recrystallization of the soap, and the properties of the grease can be altered over a wide range by suitable adjustment of the factors during the recrystallization.

Introduction

Considerable study has been devoted to solution and crystallization of sodium soaps in water, and the effect of certain variable physical factors on the particle size and form of the crystallized soap is well known. Such studies are complicated by effects attendant on the strongly ionizing medium, and various ionic equilibria and Donnan membrane phenomena must be taken into account. Consideration must be given to the probability of existence of charged micelles consisting of colloiddally dispersed soap and soap ions, and also of acid soaps.

The situation is quite different in the case of organic media, where the dielectric constant is so low as to obviate these difficulties entirely, and the conditions are so simple as to render very much easier the interpretation of the experimental results. No comprehensive investigation of the crystallization of sodium soaps in organic media has been reported. Several previous workers (1, 8, 10) have dealt with the gelation or non-gelation of soaps in these media, and some probable factors in the structure of such gels (10).

Sodium soap dispersions in mineral oils are widely used industrially as lubricating greases, and the present study forms a part of an extensive investigation of such systems. These materials are prepared essentially by heating a suspension of crystalline sodium soap in mineral oil to a suitable temperature and then allowing the mixture to cool. The crystalline soap thus obtained may differ markedly in form from the original, and the manufacture of a sodium soap grease may therefore be regarded as a recrystallization. The soap-oil dispersions vary greatly in structure and physical properties, depending on the conditions of preparation, and these factors are discussed separately.

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The effect of the use of a shearing stress during crystallization is of particular importance, and therefore the results of the variable factors entering into the recrystallization are given both where shearing forces were used and also where such forces were eliminated as far as possible.

Factors in Recrystallization

A. NO EXTERNAL SHEARING FORCE

Rate of Cooling

The general effect of the rate at which a solution is cooled on the crystal size produced is well recognized in a variety of systems. Both velocity of nuclei formation and velocity of crystallization pass through maxima as the dispersion is cooled, and the resultant crystalline phase may be obtained over a very great range of particle size depending on the rate of cooling. Extremely rapid cooling brings the system quickly to a temperature where velocity of crystallization is very low, and this is particularly marked where the liquid medium possesses a high viscosity. The converse is also true.

If a suspension of sodium soap in a mineral oil is heated until homogeneity is attained, and is then cooled rapidly, a clear hard gel is obtained. Microscopic examination shows no evidence of any soap fibres. The gels are quite stable, and no syneresis of oil is observed on allowing such gels to stand over extended periods. The system is purely lyophobic, and there is no possibility of crystal growth and consequent syneresis, owing to the lack of solubility or even wetting power (6) between the two phases. It is apparent that a structure exists, consisting of an interlacing mesh-work of extremely finely divided soap crystals, holding oil in the interstices. In view of the fact that mineral oil does not wet soap, no appreciable degree of adsorption is possible. It is therefore not possible to explain the oil-retention power of the soap in a soap-oil gel on the basis of sorption. The liquid retention must be virtually a purely mechanical one, the oil simply occupying the space available among the crystallites of the soap. With sufficiently finely divided soap, a firm stable gel can be produced with 3% of soap or less. Syneresis can arise only as a result of the collapse of the scaffolding structure where a very low concentration does not give sufficient junction points, or from ordinary seepage of oil through interstices that are too large.

Rapid cooling brings about a finely divided gel also in the case of sodium oleate, and little difference is observed with oils of varying polarity as represented by their viscosity indices. The presence of various addition materials has also little effect.

If a soap suspension in oil is heated until a homogeneous mixture is obtained, and the system is then cooled slowly, quite different results are obtained in the presence of additives. The velocity of crystallization is high, and the particle size of the solid phase and properties of the crystalline suspension now depend markedly on other factors. The results obtained on slow cooling are therefore shown in the discussion of the other factors in the following sections.

Acidity and Alkalinity of the Soap

Under conditions of rapid cooling, acid and alkaline soaps behave similarly to neutral soaps, i.e., the mixture forms a clear hard gel. On slow cooling, e.g., at the rate of $10^{\circ}\text{C. per hr.}$, neutral or alkaline sodium stearate also crystallizes in much the same condition from oil. It has been shown (3) that the temperature at which sodium stearate undergoes transitions to various mesomorphic forms is unaffected by a non-polar oil. The oil acts merely as an inert diluent and the lyophobic crystals show little tendency to grow even under conditions where the velocity of crystallization should be great. A transparent hard gel is produced and microscopic examination showed no evidence of a solid phase.

In the presence of appreciable quantities of free fatty acid, however, the results are quite different. After slowly cooling a soap-oil mixture containing free fatty acid, the soap crystallizes out in the form of fibres, which increase in length as the amount of free fatty acid increases. These fibres are capable of enmeshing considerable quantities of oil, and at the same time yield physical properties in the suspension which are desirable in industrial application. Fatty acid has been shown (2) to affect the temperatures at which transition to mesomorphic states takes place in the soap.

It is interesting to note also that the addition of fatty acid retards syneresis of oil from a soap-oil-glycerol gel and also retards the displacement of glycerol by oil, previously described (6).

Additives

Glycerol is of particular importance in this connection since a large proportion of the soap used in the manufacture of lubricating greases is made from fats. If a soap-oil mixture containing glycerol is heated to homogeneity and then rapidly cooled, the glycerol exerts only a very minor effect. On slow cooling, however, the soap crystallizes out in fibres, the dimensions of which depend on the amount of glycerol present. The following experiments show some results obtained.

Suspensions of 2 gm. of neutral sodium stearate were prepared in 18 gm. of 900 vis. 95 V. I. oil, and the following percentages of glycerol were added, based on the soap: 0, 3.5, 7, 10, 28, and 35. The mixtures were heated to 225°C. , and allowed to cool at the rate of $10^{\circ}\text{C. per hr.}$ The volume occupied by the settled crystals was found to increase with increase in amount of glycerol present. Microscopic observation, using the dry slide technique (7), showed that the fibres remained relatively small in size up to 7% of glycerol, with a very large increase using 10% of glycerol, and relatively small further increases at still higher concentrations. A similar series prepared in 100 vis. 95 V. I. oil required less glycerol for good fibre length, and it is apparent that the viscosity of the oil has an effect. The long soap fibres that settle out of the medium under these conditions readily enmesh the supernatant oil when the system is mixed. The stability of a suspension prepared in this way is fully equal to one prepared in the usual way with agitation during cooling.

Water has essentially the same effect as glycerol in bringing about the growth of large crystalline fibres on the slow cooling of a soap-oil system. Other hydroxy compounds, e.g., ethylene glycol, trimethylene glycol, erythritol, etc., are also effective in promoting long fibre formation in the recrystallization of soap from mineral oil. These additives differ somewhat in the maximum temperature to which the system must be heated prior to crystallization.

Nature of the Oil

The oils used as media for the recrystallization of soap may vary in two important respects, viz., (i) viscosity and (ii) polarity, as represented by the viscosity index. Two series of recrystallizations were carried out, the first using sodium stearate containing 0.5% free fatty acid and the second using sodium stearate containing 0.5% free alkali. The results were identical for each series. In each experiment, 1 gm. of the soap, together with 0.1 gm. of glycerol, was suspended in 20 gm. of the oil and the mixture was heated to 190° C. The homogeneous system was then allowed to cool at the rate of 10° C. per hour, without agitation. Samples were then examined in the microscope between crossed Nicols. Table I shows the results obtained.

TABLE I
EFFECT OF OIL MEDIUM ON RECRYSTALLIZATION

Oil	Fibre length	Texture of suspension
330 vis. 40 V.I.	Good	Fibrous
750 vis. 40 V.I.	Fair	Fairly fibrous
100 vis. 70 V.I.	Very short	Dry and granular
150 vis. 70 V.I.	Very short	Dry and granular
300 vis. 70 V.I.	Very short	Low consistency
450 vis. 70 V.I.	Very short	Low consistency
200 vis. 75 V.I.	Very short	Low consistency
190 vis. (at 210° F.) 80 V.I.	No fibres visible	Very low consistency

It is noted that long fibres were obtained only with oils of 40 V.I., and that a lower viscosity for the same V.I. yielded a longer fibre. The oil termed 190 vis. (at 210° F.) 80 V.I., with the highest V.I. and highest viscosity, yielded crystals so small that they were not resolvable in the microscope. It is apparent that the polar constituents of the low V.I. oil act in a manner somewhat similar to glycerol and other additives in producing long fibre soap crystals on recrystallization.

Soap Concentration

It is apparent that the concentration of the phase to be crystallized will have an effect on the size of the crystals produced. Suspensions containing equal proportions of sodium stearate and sodium oleate, together with 10% of glycerol based on the soap, were made up in 200 vis. 75 V.I. oil to the following concentrations expressed as percentage soap by weight: 36, 22, 16, 11, 8.5, 7.

1. The suspensions were heated to 160° C. for two hours, and then cooled at 10° C. per hr. Microscopic examination showed that only the most concentrated suspension contained soap fibres.

2. The suspensions were reheated to 174° C. for one hour, and then cooled at 10° C. per hr. Microscopic examination showed that all excepting the most dilute suspension now showed recrystallized long fibres.

3. The suspensions were reheated to 183° C. for one hour, and then cooled at 10° C. per hr. All the suspensions now showed recrystallized long fibres on microscopic examination between crossed Nicols.

A possible explanation of these results might be advanced as follows. The soaps undergo transitions through several mesomorphic states reaching, in the case of sodium stearate, a plastic state at about 125° C. Above that temperature, the soap is probably polydisperse, and the degree of dispersion is probably statistically distributed according to a Maxwell distribution curve. Only a range of highly dispersed soap is capable of undergoing recrystallization on cooling. At 160° C., only the most highly concentrated of the above suspensions possessed a sufficiently highly dispersed soap to produce long fibres on cooling. At 174° C., the distribution curve of particle size has been displaced so that the proportion of soap within the range of very highly dispersed material is considerably increased. After heating to 174° C., therefore, all the suspensions down to 8.5% concentration show recrystallized long fibres on cooling. Heating to 183° C. increases likewise further the amount of highly dispersed soap available for recrystallization, and after heating to this temperature the most dilute of the suspensions used also shows recrystallized fibres on cooling.

Combined Water in the Soap

Sodium stearate, dried at 105° C., contains about 6% of water, which is apparently combined by moderately strong adsorptive forces to the soap. The monohydrate corresponds to 6%. Vold and Ferguson (11) concluded that there is no hydrate of sodium palmitate, since no discontinuities were obtained in the vapour pressure curve.

Lawrence (9) has assumed hydration, and found that the "hydrated" soap gelled on cooling from suspension in mineral oil. On the other hand, sodium stearate prepared by him from stearic acid and sodium was found to crystallize out without gelation. Correspondingly, he found a discontinuity in the cooling curve only with the hydrated soap.

In the present work, the following experiments were carried out in this connection. An excess of metallic sodium was added to a solution of stearic acid in 330 vis. 40 V.I. oil, and the mixture was heated to about 150° C. On cooling, the sodium stearate formed set to a gel. Similar gels were prepared in oils of 75 V.I. and 95 V.I. Sodium oleate also yielded gels when prepared in this fashion. It was then considered possible that air might be occluded in the system, and traces of water might thus be produced through the interaction of sodium oxide and the fatty acid. In order to preclude this possibility

entirely, the following experiment was carried out. A glass vessel was constructed having three compartments such that the contents of the three sections could be mixed by pouring together while the whole vessel was under vacuum. In this apparatus, a mineral oil was brought to boiling under vacuum, stearic acid was melted under vacuum, and clean sodium was also melted under vacuum. The three constituents were then mixed by pouring them together while still under vacuum. On cooling, a gel was formed.

The writers have therefore found that water is not necessary for the process of gelation of soaps in oil. It would appear also, in contradiction to the findings of Lawrence (9), that alkali soaps are stable and show no tendency to decomposition in the absence of water. The 6% of water is undoubtedly quite strongly adsorbed, but could probably be largely removed by heating the soap *in vacuo*.

B. WITH EXTERNAL SHEARING FORCE

The experiments described above were carried out without agitation. The manufacture of sodium soap greases is carried out industrially by dispersing the soap in oil in large steam-jacketed kettles fitted with double-action agitators. The clearance between opposing vanes of the agitator is relatively small, and care is taken to add the oil slowly so as to maintain a high concentration of soap during the addition of the first portion of the oil, i.e., during the formation of the concentrated suspension.

A grease kettle of about one pound capacity was constructed, similar in most respects to the usual kettle of industrial size. It consisted essentially of a stainless steel cylindrical vessel welded into a surrounding oil-bath also of stainless steel. The oil-bath was fitted with a cooling coil and was so arranged that either gas or electrical heating could be used. The inner vessel was fitted with a double-action stirrer, i.e., with adjacent vanes revolving in opposite directions, driven through a gear system from a motor and speed reducer. This apparatus was used for the preparation of sodium soap greases in the laboratory, simulating conditions on a large scale.

Variation in the factors of rate of cooling and concentration of soap was found to produce results essentially similar to those obtained in the recrystallization without shear.

Micro-preparations of Soap-Oil Dispersions

For the preparation of soap-oil dispersions on a micro-scale, a microscope slide was wrapped with nichrome ribbon, leaving a small area at the centre for observation. The heating element was fed from a 110 volt line through a variable resistance so that the rate of heating could be varied, and positions on the rheostat were calibrated to the corresponding temperatures. The actual temperature of the material under observation was read by means of an iron-constantan thermocouple attached to a sensitive low temperature pyrometer. The thermocouple was so constructed as to serve at the same time as a hand stirrer for agitation of the soap-oil mixture. The slide was insulated from the stage by asbestos sheet and clamped into place.

A small quantity of a mixture of sodium oleate and 900 vis. 95 V.I. oil was placed on the slide and heating begun. Observation was made throughout at a magnification of only 30 diameters in order to preserve a relatively large field. The soap showed a sudden large swelling at about 70° C. It was noted, however, that most of the oil remained free, and that the mixture was not plastic. On continued heating, the suspension attained some plasticity at about 150° C.

This procedure was repeated using a mixture of sodium oleate and 900 vis. 40 V.I. oil. In this case, also, sudden swelling of the soap was noted at 70° C., but on continued heating the mixture became highly plastic quite sharply at about 95° C. At this stage, movement of one portion of the material by the thermocouple drew almost the whole mass with it, and fibres could be drawn out readily. The plasticity was retained over a considerable further increase in temperature, following which the viscosity decreased rapidly.

A mixture of neutral sodium stearate and even a low V.I. oil, e.g. 900 vis. 40 V.I. oil, did not attain plasticity up to 150° C. On addition of a small proportion of glycerol, however, the mixture showed very high plasticity at a relatively low temperature, which depended on the quantity of glycerol added. Soap fibres could be drawn out only where a good degree of plasticity had been attained. The term plasticity is used here in the sense that the application of an external force to a portion of the material results in a strain over portions of the sample relatively far removed from that point of application.

It is noted therefore that the unsaturation of the soap, the polarity of the oil, and the presence of an additive such as glycerol, are important factors in bringing about a state in the suspension, such that shearing forces are effective in the production of long soap fibres. This constitutes a recrystallization of the soap, not from a very highly dispersed melt in the oil, but rather from a mesomorphic state at a temperature much below that used in the earlier section of this work on recrystallization without shear. The interpretation of these results is left for the later section on discussion.

Torsional Viscometry in Soap-Oil Suspensions

The distribution of a shearing stress over a large area, as described above, was found to be illustrated well by a simple type of torsional viscosimeter. A 150 cc. Pyrex beaker was fitted with three short lengths of glass rod sealed in staggered position on the inside of the beaker. These, together with the two vanes of a glass stirrer driven by a constant speed stirring motor, formed the agitating system. The bottom of the beaker was sharply indented inwards at the centre, and this indentation was seated on the point of a thumb-tack so as to provide a low friction bearing. The beaker and support rested in an oil-bath heated by a Bunsen burner. Near the top of the beaker, there was sealed a small glass hook to which was attached a thread, which in turn was attached to a low-tension spring fixed at the other end. The agitation of the soap-oil mixture in the beaker created a torque that was

taken up by the spring, and this torque was measured by a pointer on the spring and a millimetre scale fixed below the spring. The temperature was read by means of a thermocouple used in conjunction with a low-temperature pyrometer.

An increase in the viscosity of the soap-oil system resulted in an increased torque which could be measured. A concentration of 20% of soap was found to yield good results. Constant rates of heating were used. After reaching the maximum temperature used, the suspension was cooled slowly, and the dispersion was examined in the microscope by the dry-slide technique (7).

1. *Sodium Stearate*.—Neutral sodium stearate and 900 vis. 95 V.I. oil showed no large increase in viscosity up to 205° C. The soap crystallized out on cooling, and no fibres were obtained. Similar results were obtained on the addition of 10% of stearic acid (based on the soap). With 900 vis. 40 V.I. oil, a sudden large increase in viscosity was obtained at about 160° C., and, after further heating to 205° C. and cooling, the soap was found to be recrystallized to fibres of fair length. A mixture of neutral sodium stearate and 900 vis. 95 V.I. oil, together with 6% of glycerol (based on the soap), showed a sudden large increase in viscosity at about 95° C., and after further heating and subsequent cooling long fibres were noted.

2. *Sodium Oleate*.—Neutral sodium oleate and 900 vis. 95 V.I. oil showed a very slight increase in viscosity at about 100° C. and short fibres were noted on cooling. The addition of 10% of glycerol (based on the soap) reduced this temperature to about 90° C., and short fibres were again obtained on cooling. Neutral sodium oleate and 900 vis. 40 V.I. oil showed a sudden very large increase in viscosity at 60° to 70° C., and, on cooling, fibres of good length were noted.

3. *Various Addition Agents*.—A 20% suspension of sodium stearate (0.5% of F.F.A.) in 900 vis. 95 V.I. oil was treated with 10% (based on the soap) of various addition agents. Glycerol produced a sudden increase in viscosity at about 95° C., and on cooling from this temperature short fibres were noted. With phenol, the mixture wound completely around the stirrer at 170° C., and on cooling a very long fibred grease was obtained. This effect was somewhat reduced in the series through pyrocatechol and resorcinol, and hydroquinol produced no increase in viscosity and no fibres on cooling. Propylene glycol, trimethylene glycol, ethylene glycol, erythritol, and water were all found to show increases in viscosity, and produced fibres on cooling. The temperature range over which plasticity is attained varies with the addition agent used.

Nature of the Oil

Some results on the effect of the V.I. of the oil on recrystallization to long fibres have already been noted. Further experiments were carried out in the laboratory-scale grease kettle, where a maximum temperature of 160° C. was used. Under these conditions, sodium stearate showed no plasticity in the following oils: 300 vis. 95 V.I., 100 vis. 95 V.I., 330 vis. 40 V.I., 100 vis.

40 V.I. There was no recrystallization to fibres on cooling. The addition of glycerol resulted in fibre formation with each oil. A 50 : 50 mixture of sodium stearate and sodium oleate showed no plasticity with 300 vis. 95 V.I. oil, and a plastic range beginning at 103° C. with 300 vis. 40 V.I. oil.

The effect of V.I. was further investigated as follows. A 300 vis. 40 V.I. oil was treated with 30% by weight of 96% sulphuric acid at 40° C. for a few minutes, and then the mixture was allowed to stand at room temperature overnight. The oil was then decanted and treated under the usual "contacting" conditions with acid activated bentonite. The V.I. was raised from 40 to 58 by this refining treatment. A 50 : 50 mixture of sodium stearate and sodium oleate and this treated oil showed a plastic range beginning at 140° C., as compared with 103° C. prior to refining of the oil. It is apparent that the removal of the oil constituents most readily attacked by sulphuric acid results in a considerable decrease in the property of the oil that brings about swelling and plasticity of the soap on suspension.

Stages Observed in Recrystallization

A recrystallization was carried out in several steps under controlled conditions in the laboratory-scale grease kettle described above. During the course of the preparation, samples were withdrawn at intervals and photomicrographs prepared by the dry slide technique (7). Since rapid transfer from the mix to the microscope slide is equivalent to very rapid cooling, the sample was maintained essentially in the condition which obtained in the mix at the stage at which it was withdrawn.

Sodium stearate (80 gm.) (10% of F.F.A.) and 75 gm. of 70 V.I. oil were heated to 163° C. with agitation. Then the remainder of the oil was added slowly with agitation as the temperature was allowed to decrease. The temperature was 96° C. when all the oil had been added and the soap concentration was 16.5%. (Sample taken—Fig. 1). After the addition of 3.75% of glycerol, based on the soap, the mixture was maintained at 96° C. for two hours with agitation. (Sample taken—Fig. 2). A further 2.75% of glycerol was added and the mixture maintained at 96° C. for a further 1.5 hr. with agitation. (Sample taken—Fig. 3). Additional glycerol was added to a total of 9% based on the soap, and the mixture was maintained for two hours more at 96° C. (Sample taken—Fig. 4). The suspension was then allowed to cool slowly overnight, and it showed evidence of being slightly fibrous in texture. The mixture was then heated to 190° C. where it appeared completely melted and homogeneous. (Sample taken—Fig. 5). From this maximum temperature, the mixture was slowly cooled and samples were taken during cooling at the temperatures noted below. Agitation was maintained throughout.

160° C. — Fig. 6

121° C. — Fig. 7

80° C. — Fig. 8

50° C. — Fig. 9

PLATE I

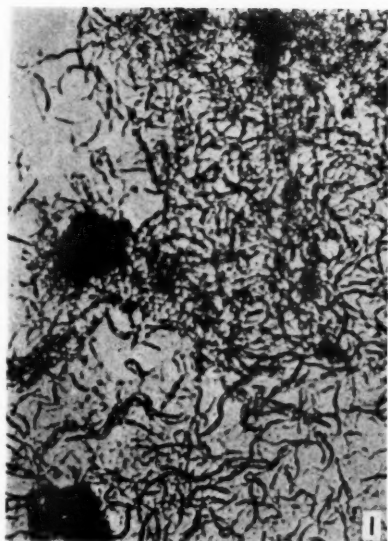


PLATE II.



PLATE III

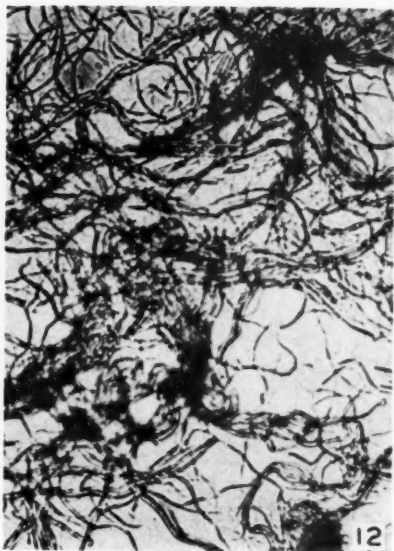
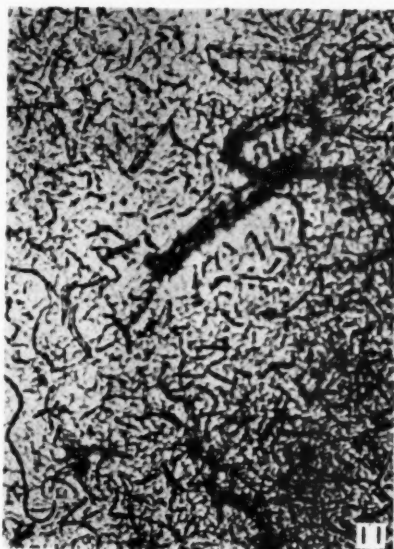
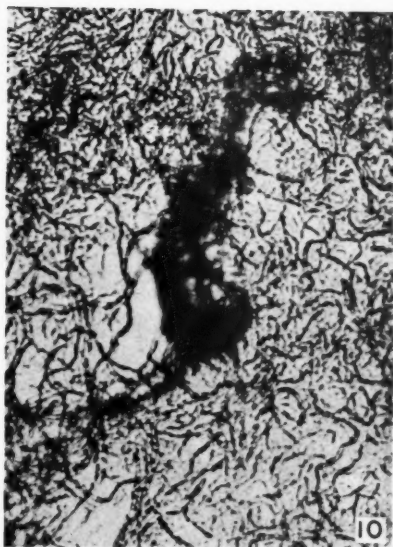
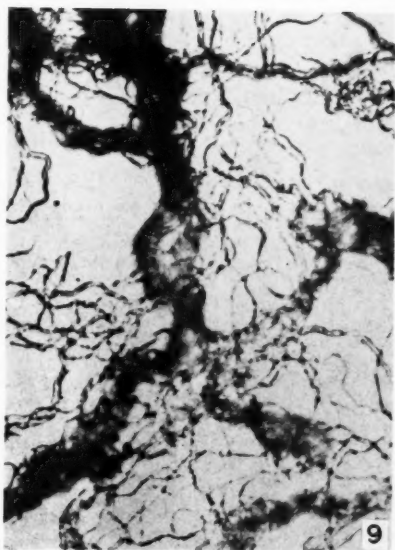
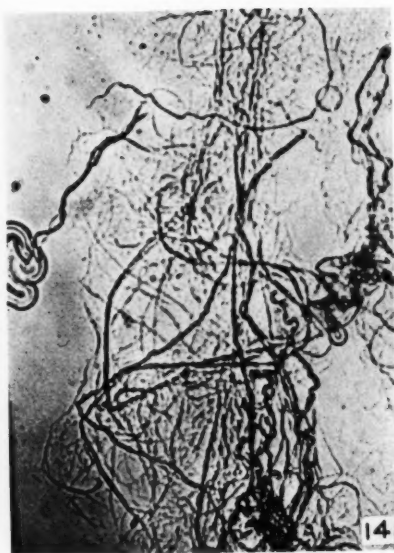
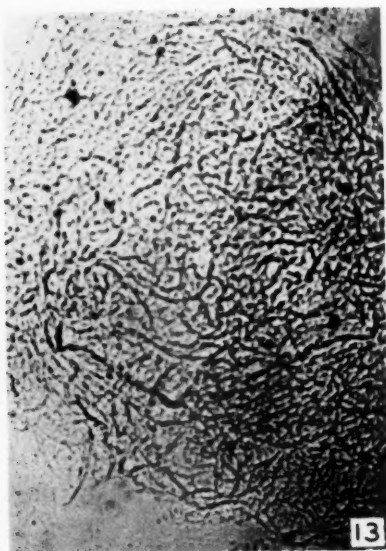


PLATE IV



The suspension was then allowed to cool further to room temperature. Figs. 10 and 11 represent samples taken after 0.5, 1, and 2 hr. agitation at room temperature, respectively. The suspension was then reheated to 172° C. and cooled slowly to room temperature. (Sample taken—Fig. 12).

The effects of the quantity of glycerol present, the temperature and the rate of cooling are well exemplified in the above series. Fig. 1 shows very short fibres only in the absence of glycerol. It is probable that the acidity of the soap accounts for fibres of even this size on recrystallization. With increasing quantities of glycerol, Figs. 2, 3, and 4 show progressively increasing extent of fibre formation. After the material had been melted and cooled rapidly very small fibres were obtained (Fig. 5). Figs. 6, 7, and 8 show a progressive increase in fibre size with increased cooling. The disruptive effects of agitation at low temperatures are observed in Fig. 9. Figs. 10 and 11 are representative of a larger number of photographs showing further extensive breakdown of the fibrils, the effect decreasing as the fibrils become short. Fig. 12 represents a slow recrystallization from a relatively high temperature.

The growth of the soap fibres during recrystallization was further noted in a long-fibred sodium soap lubricating grease of commercial manufacture. The sample was melted by heating to 220° C., and then allowed to cool at 10° C. per hr. Samples were withdrawn at various temperatures and photomicrographs prepared by the dry slide technique. The following illustrate results obtained.

220° C. — Fig. 13

168° C. — Fig. 14

150° C. — Fig. 15

112° C. — Fig. 16

Fig. 13 shows very short fibres on rapid cooling from solution. The progressive increase in fibre dimensions is shown in the remainder of this series. On cooling further, the material resembled closely the original sample of grease used.

Structural Viscosity in Soap-Oil Suspensions

Measurements of structural viscosity, or change in viscosity with shearing stress, were carried out in a specially designed efflux viscosimeter, with provision for the alteration of the driving pressure. Viscosity measurements were made over a range of pressures at each temperature, both on heating the suspensions and during cooling. The maximum temperature used was 160° C. A summary of the results is given below.

On heating a suspension of sodium stearate or oleate on a non-polar oil (95 V.I.), no structural viscosity could be detected. The viscosity curve was found to be essentially parallel to that shown by the oil alone; the small increment in inner friction caused by the soap was merely a function of the volume occupied by the solid phase. Up to 160° C., the suspensions remained cloudy and there was no departure from Newtonian flow, denoting no varia-

tion in the form of the dispersed phase and in the relation between dispersed phase and medium. With sufficiently high temperature, the soap eventually melted, with consequent increase in viscosity. On cooling such a melted dispersion in a high V.I. oil, it was found that the system was completely reversible. Such a system is therefore essentially lyophobic in nature, and the soap-oil mixture showed no attraction between medium and dispersed phase.

On heating a suspension of soap in a polar oil (40 V.I.), on the other hand, quite different relations were found. These dispersions become visually homogeneous at an intermediate temperature. At driving pressures below about 6 cm. of mercury, sharp increases in viscosity were obtained, and a high degree of structural viscosity was shown. On cooling, the viscosity increases continuously until the system attains the consistency of a paste or hard gel, depending on the rate of cooling. It is apparent that this system is lyophilic and the form of the disperse phase is strongly affected by the medium.

Discussion

Recrystallization of sodium soaps involves a disruption of the original crystals followed by re-orientation of the dispersed molecules or groups of molecules to a newly formed crystalline phase. The lattice forces may be overcome either by melting or by solvent action, or a combination of the two. As a result of their bipolar nature, sodium soaps have been shown (2) to undergo transitions through various mesomorphic states. Partial melting in one or two lattice dimensions results in a change of state with consequent changes also in solubility considerations.

When sodium stearate is heated in a non-polar mineral oil, the medium behaves inertly until a high temperature is reached. At the bidimensional melting point (3), about 100° C., the polar bonds between adjacent sodium carboxylic groupings are unaffected, and the non-polar mineral oil has no swelling action on the soap. The hydrocarbon chains of the soap are not dissolved by the oil. Above 160° C. a large swelling action is noted, owing probably to a sufficient proportion of the very highly dispersed soap formed. The soap eventually melts to a liquid-crystalline state just as in the case of soap alone. On cooling, the soap passes through the same physical states and crystallizes out in small crystals. Surface tension measurements show (4) that the non-polar oil does not bring about a high degree of dispersion by solvent action, and viscosity measurements in the present work indicate that the system is essentially lyophobic. The non-polar mineral oil does not wet the soap at low temperatures (6), and the soap shows a low sedimentation volume in that medium (5). The same holds true for sodium oleate, with due regard to the lower transition temperatures. The application of a shearing force during recrystallization has no effect since the soap particles are not swollen, and the force is not transmitted through a lyophobic system.

Recrystallization of a sodium soap from a non-polar mineral oil, e.g. 95 V.I., must therefore be regarded as a crystallization from a hot melt, with virtually no solvent action by the medium.

When sodium stearate is heated in a more polar mineral oil, quite different results are obtained. At the bidimensional melting point of the soap, the latter swells in the medium. The polar sodium carboxylic groupings are partially disrupted by the polar constituents of the oil, and the medium can now exert a solvent effect on the hydrocarbon chains of the soap. It may be expected that some structure remains and this is shown by swelling rather than ordinary solution without swelling. The suspension now shows a high degree of structural viscosity, since shearing forces will be able to parallelize the dispersed particles and exert a streamlining effect leading to a reduced viscosity. The application of an external force results in a distribution of the stress over a large area, where the concentration is sufficiently great to yield a tangled mass of dispersed particles which are highly lyophilic to the medium. It is noted therefore that shear is of importance in the recrystallization of a sodium soap from a polar mineral oil, since the suspension is such that orientation of dispersed groupings are possible. Such an orientation is probably the first step in the formation of a large soap fibre (7). Sodium oleate has a low bidimensional melting point and plasticity point (2), and shows a very large degree of swelling in a non-polar oil. The fibre length obtainable on recrystallization is correspondingly very great.

A number of polar additives, notably glycerol, produce effects that are apparently similar to those of a polar oil. When a sodium soap is heated in a non-polar oil in the presence of glycerol, the soap swells at a low temperature depending on the amount of glycerol present. Swelling may begin at the unidimensional melting point (3). The system is now lyophilic, and shearing forces can play a large part in orientation of the soap micelles, with consequent ease in recrystallization to long fibres.

This recrystallization may be regarded as a dual type, partaking of the characteristics of both the hot melt and solvent type. A moderate degree of heat is necessary to disrupt the secondary valencies holding the hydrocarbon chains of the soap in the lattice. Solvent action is then obtained by the use of glycerol or the polar constituents of a low V.I. oil. At this stage, the application of a shearing stress can exert an orientating action to produce fibrils. With lowering in temperature, the glycerol or other addition agent is displaced (6), and the soap crystallizes as the bidimensional and unidimensional solidification points are reached. If no shear is used, little or no fibres are produced even in the presence of the polar addition agents at the relatively low temperatures which suffice when shearing forces are applied. In the absence of these stresses, the mixtures must be brought to much higher temperatures, e.g., 200° C. for sodium stearate, in order to effect a solution of the soap, which can then crystallize to long fibres on cooling. The use of orientating forces takes the place therefore of a higher degree of dispersion prior to recrystallization.

Acknowledgment

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THE EFFECT OF HIGH SHEARING STRESSES ON RECRYSTALLIZATION OF SODIUM SOAPS IN MINERAL OILS¹

BY WILFRED GALLAY² AND IRA E. PUDDINGTON²

Abstract

High shearing stresses obtained by use of the colloid mill are shown to bring about recrystallization of sodium soaps at temperatures above the plasticity point of the soap. Below this temperature a comminuting action only on the soap in suspension is obtained. The length of soap fibre produced in the recrystallization increases with increase in polarity of the oil and with decrease in viscosity of the oil. The fibre length increases particularly markedly with increase of degree of unsaturation of the soap. The addition of glycerol or fatty acid has little effect.

The action of the shearing stress is discussed and it is concluded that long crystals are produced by a shearing of the double soap molecules on slip planes between melted hydrocarbon chains. The recrystallization is thus induced on molten portions of the soap.

A previous communication (3) dealt with the effect of various factors on the recrystallization of sodium soaps in mineral oils. Relatively small shearing stresses, e.g., by single or double-action stirrers, applied during recrystallization, were shown to have an appreciable effect on the production of long crystals and hence also of long fibres in the resultant system. The present work deals with the application of high shear in such recrystallizations by use of the colloid mill.

When a suspension of sodium soap in a mineral oil was passed through a colloid mill at ordinary temperature, it was found that the product was merely a well dispersed suspension. No action was produced on the soap other than a simple grinding to smaller particles. It was then found that if the suspension was preheated to a minimum temperature, depending on the nature of the soap and the oil, a recrystallization of the soap could be effected by passage through the colloid mill. These minimum temperatures of preheating found necessary corresponded closely to the swelling temperature of the soap-oil system. The swelling temperature was determined by gradually heating a 20% suspension of the soap in oil, and noting the temperature at which an increase in viscosity of the system was observed. It was found that this point could be determined closely, and repeat experiments showed satisfactory precision. Table I shows the results obtained.

It is noted that sodium stearate shows essentially the same swelling temperature over this very wide range of polarity of the oil used, whereas, with sodium oleate, there is a progressive decrease in swelling temperature with increasing polarity in the oil.

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² Chemist.

TABLE I
SWELLING TEMPERATURE OF SOAP-OIL SUSPENSIONS

Soap	Oil	Swelling temp., °C.
Sodium stearate	300 vis. 95 V.I.	125
Sodium stearate	300 vis. 70 V.I.	120
Sodium stearate	300 vis. 40 V.I.	120
Sodium stearate	1200 vis. -95 V.I.	120
Sodium oleate	300 vis. 95 V.I.	105
Sodium oleate	300 vis. 70 V.I.	90
Sodium oleate	300 vis. 40 V.I.	75
Sodium oleate	1200 vis. -95 V.I.	60 - 65

Any soap-oil system must therefore be preheated to its swelling temperature, prior to recrystallization by high shear in the colloid mill. This temperature corresponds closely to the plasticity point (1) of the soap, denoting a physical state in which bidimensional melting of the soap is essentially completed.

The length of the recrystallized soap fibres produced was found to vary markedly with the nature of the soap and oil used. The various systems investigated were preheated to 125° C., and passed once through a laboratory colloid mill. The fibre length of the resultant viscous grease was determined by two methods, viz., hand and machine. The hand evaluation is qualitative and is carried out by drawing out fibres with the finger-tip from a sample on the palm of the hand, or between finger-tips. Some experience in handling these systems is necessary for such evaluation, but the method is included since it is commonly used in industry. The machine evaluation of fibre length was carried out by means of a fibre-pulling apparatus previously described (4). The data obtained in this way show well the comparative order of fibre length and are not intended for use as absolute values. In view of the fact that orientation and further fiberization of smaller fibres proceeds during the drawing-out process, such data can have no meaning as absolute values.

The soap concentration was 9% throughout. Table II shows the results obtained, and Figs. 1 to 12 show photomicrographs of corresponding samples. The table is arranged to show the effect of various factors separately.

The length of the fibres formed by recrystallization through high shear varies markedly with the properties of the constituents. Increase in polarity of the oil, as represented by decrease in viscosity index, results in increase in fibre length. Decrease in viscosity of oils of the same polarity results also in greater fibre length. The latter increases particularly markedly with increased degree of unsaturation of the soap. This is shown not only in Series A and B of Table II, but particularly in the last experiment noted where an unsaturated soap in an oil of low V.I. and low viscosity yielded the longest fibres in the whole series. Figs. 1 to 12 show photomicrographs of these suspensions, prepared by the dry slide technique (4).

PLATE I

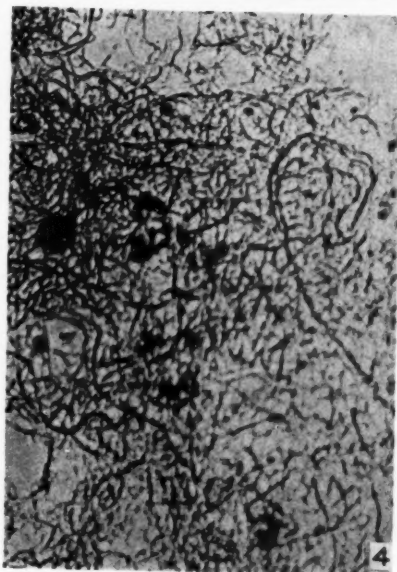
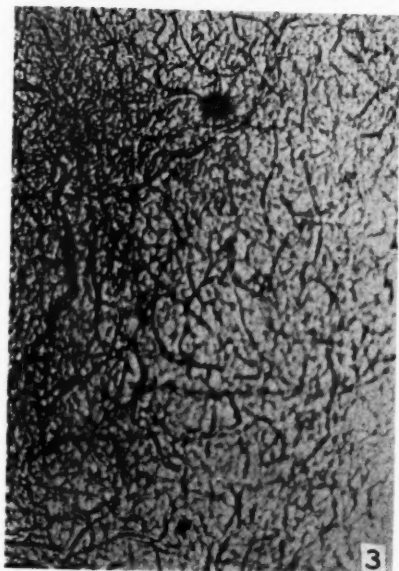
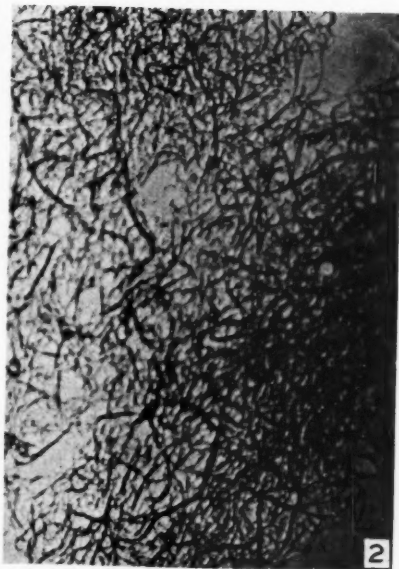
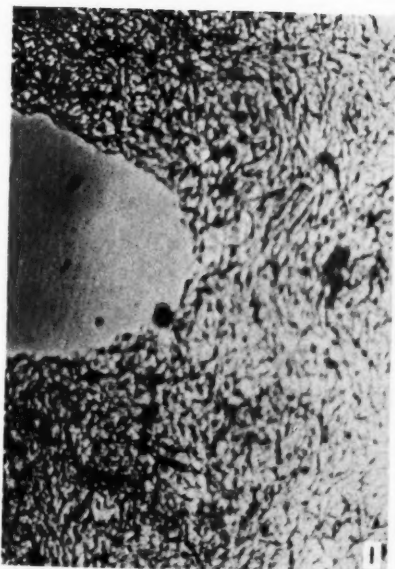


PLATE II

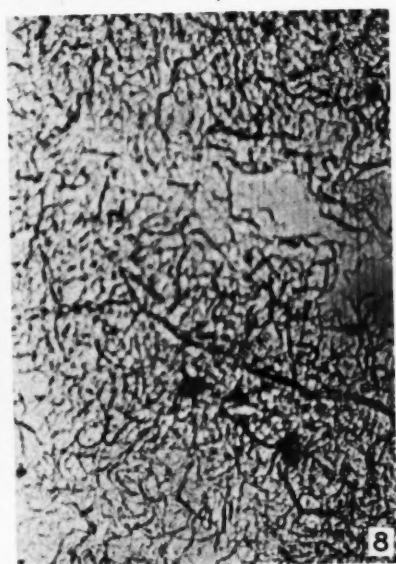
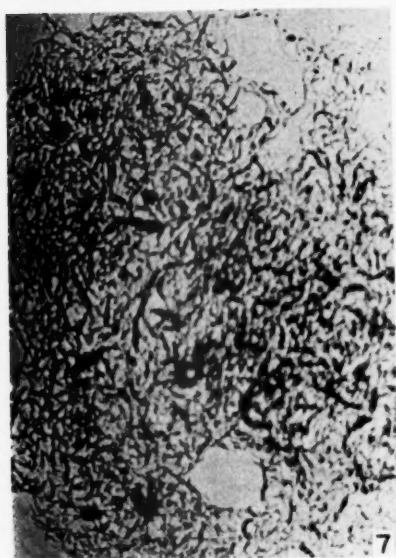
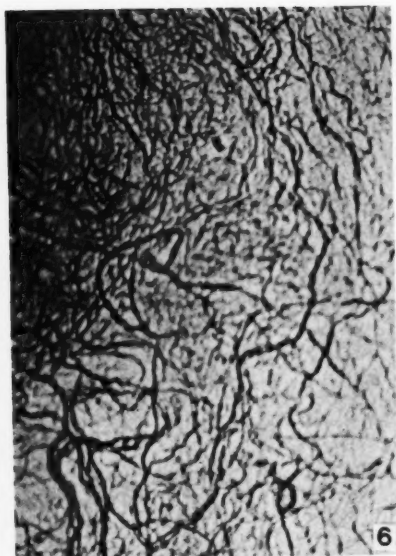
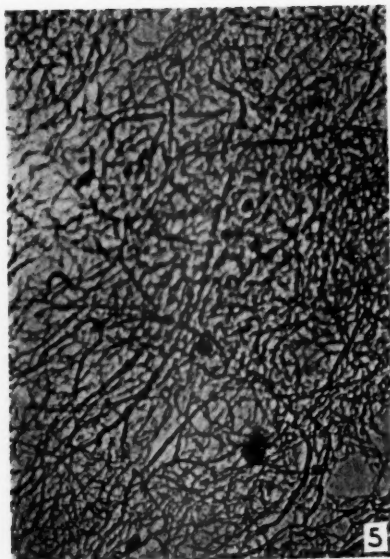
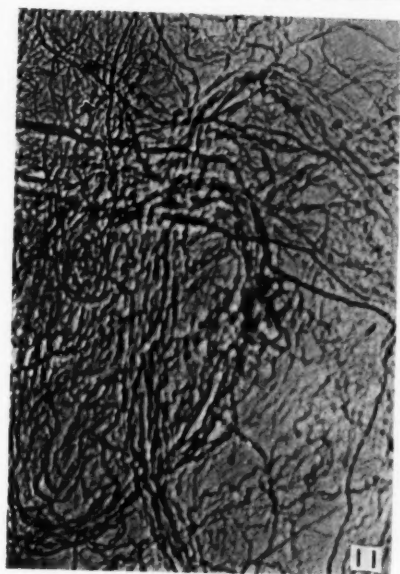
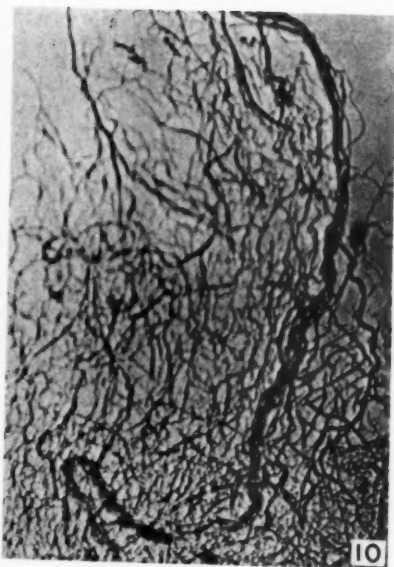
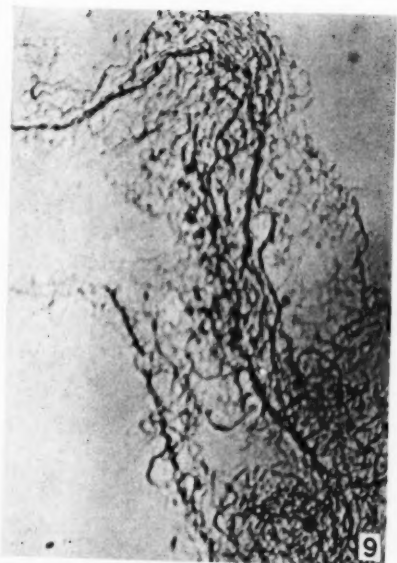


PLATE III



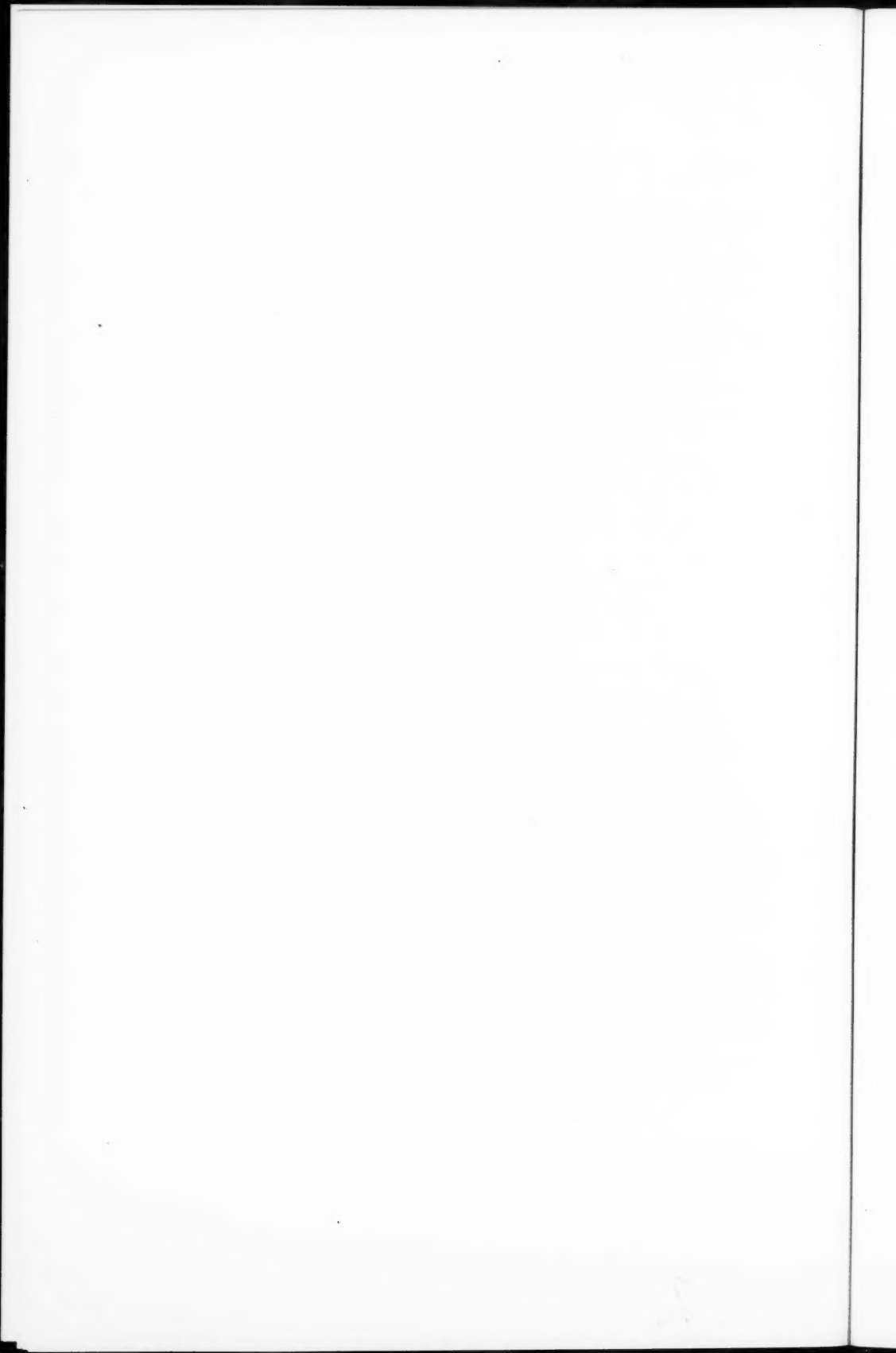


TABLE II

FIBRE LENGTH OF SODIUM SOAPS IN OIL RECRYSTALLIZED BY HIGH SHEAR
(Mixed soap—50 : 50 mixture of sodium stearate and sodium oleate)

Soap	Oil	Fibre length		Fig.
		By hand	By machine, cm.	
<i>A. Oils of the same viscosity, varying V.I.</i>				
Sodium stearate	95 V.I., 500 vis.	Very short	0.2	1
Sodium stearate	70 V.I., 500 vis.	Somewhat longer	0.6	2
Sodium stearate	40 V.I., 500 vis.	Still longer	1.2	3
Mixed soap	95 V.I., 500 vis.	Fairly long	0.9	4
Mixed soap	70 V.I., 500 vis.	Somewhat longer	1.3	5
Mixed soap	40 V.I., 500 vis.	Very much longer	3.0	6
<i>B. Oils of the same V.I., varying viscosity</i>				
Sodium stearate	95 V.I., 500 vis.	Very short	0.2	1
Sodium stearate	95 V.I., 300 vis.	Very short	0.2	7
Sodium stearate	95 V.I., 100 vis.	Somewhat longer	0.7	8
Mixed soap	95 V.I., 500 vis.	Fairly long	0.9	4
Mixed soap	95 V.I., 300 vis.	Slightly longer	1.1	9
Mixed soap	95 V.I., 100 vis.	Still longer	1.5	10
<i>C. Oils of low V.I.</i>				
Mixed soap	40 V.I., 100 vis.	Very long	1.9	11
Sodium oleate	40 V.I., 100 vis.	Longest of series	4.8	12

Further experiments were carried out to determine the effect of additives of importance in the industrial utilization of these systems as lubricating greases. The addition of glycerol up to 10% concentration, based on the weight of the soap, had no appreciable effect on the length of the fibres produced in recrystallization by means of the colloid mill. Variation in acidity of the soap from 0.5% F.F.A. to 2.5% free alkali likewise had no appreciable effect on the fibre length.

The colloid mill used in this work was a light duty $\frac{3}{4}$ hp. laboratory size mill intended for the preparation of emulsions. The speed of the rotor under load was about 8000 r.p.m. and the clearance was about 0.01 in., and no facilities were available for altering the clearance between rotor and stator. Comparative experiments in a larger size mill, with higher shearing stresses, under smaller clearances, showed essentially similar results.

Discussion

A crystal of sodium stearate consists of an orderly arrangement of double soap molecules in the lattice. The double molecules are at an angle to the long axis of the crystal; this results in planes of alternating polar and non-

polar bonds parallel to the long axis of the crystal. The bonds along the hydrocarbon chains and between adjacent terminal methyl groups of these chains are relatively weak, and the crystal shows unidimensional, bidimensional and plasticity points at about 70° C., 100° C., and 125° C. respectively (1). Disruption of the polar bonds, however, in the absence of solvent action, does not take place until the crystal is heated to about 200° C. (1).

Solvents may obviously be of two types, viz. (1) those affecting the non-polar hydrocarbon chains, and (2) those affecting the polar carboxylic groupings. Those of the first type have been shown to be without effect owing to the strong polar bond. Thus melting points of the soap remain unaffected in the presence of a non-polar mineral oil (2). Polar materials are capable of exerting a solvent action on the soap only after a melting of the non-polar bonds of the lattice (2). Thus water has no effect on the lattice constants of sodium stearate below 70° C. (5).

Similar behaviour is shown by sodium oleate at the corresponding temperatures of alterations in physical state for that soap.

Recrystallization of a sodium soap must involve a rearrangement of the molecules, subsequent to a loosening of the lattice bonds by solvent action or melting. In the case of solvent action, fairly long fibres may be obtained by recrystallization from a polar solvent, e.g., water. Both polar and non-polar bonds are here disrupted above the unidimensional melting point or genotypical point. With a non-polar mineral oil medium, however, it is apparent that no solvent action can be exerted and recrystallization must result from a melt. It has been shown in the present work that recrystallization can be effected by high shearing stresses at temperatures above the swelling temperature of the system. This temperature is the plasticity point of the soap (1), i.e., the lattice bonds in the two directions at right angles to the molecular axis are totally disrupted and the soap is essentially a partially melted solid having alternate planes of firmly held polar bonds between sodium carboxylic groupings (Fig. 13, *b*).

The soap is plastic at this stage (1), since planes of slippage are available between the ends of hydrocarbon chains. Shearing forces are capable therefore of displacement of planes of double molecules. In a soap-oil suspension of sufficient concentration, it is apparent that such shearing displacements will result in the overlapping of crystal planes in the direction of the shearing force, with the consequent production of crystals which are very long in one dimension. Growth of such crystals by subsequent overlapping of crystals along their length results in very long fibres (4) such as shown in Fig. 13. Here a highly diagrammatic representation is shown of four stages of a recrystallization induced by high shear in the colloid mill. One lattice plane only is drawn for simplicity. *A* represents a portion of a soap lattice at room temperature. *B* represents the condition at the plasticity point. Two of the crystal axes have disappeared as a result of melting of the non-polar hydrocarbon chains of the soap, and slip planes are available between the double molecules. *C* represents the condition after the application of a shearing

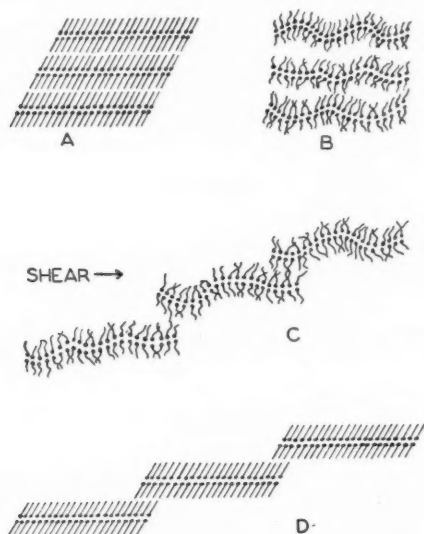


FIG. 13. Diagrammatic representation of the effect of high shearing stresses on a sodium soap in oil suspension. Circles and lines represent sodium carboxylic groupings and hydrocarbon chains of the soap respectively. A—at room temperature; B—at 125° C.; C—at 125° C. under shear; D—at room temperature after shearing.

stress with displacement of the planes in the direction of stress. D shows the condition after cooling below the unidimensional melting point. Long crystals and, subsequently, long soap fibres are produced by the recrystallization under shear.

It is apparent that shearing forces should be ineffective at temperatures below the plasticity point of the soap, and this has been shown to be the case. The magnitude of the shearing force will obviously be of importance also. Thus no recrystallization of sodium stearate in mineral oil can be effected even at temperatures as high as 160° C. where shear is applied by a double action stirrer on highly concentrated soap suspensions. It is apparent that no shear is necessary for recrystallization where a disruption of the polar bonds is involved, and long fibres can be formed in systems heated to 200° C. and allowed to cool without agitation (3).

At 160° C., the addition of a polar solvent such as glycerol exerts sufficient solvent action on the polar bonds in the soap lattice, so that recrystallization can take place even with the relatively small shearing stresses available with a double action stirrer. At 125° C. it has been shown that the addition of glycerol up to 10% concentration, based on the soap, results in no appreciable difference when high shearing stresses are used. Sufficient loosening is obtained in the slip planes between hydrocarbon chains, and the additional swelling or solvent action in the planes of the polar bonds makes little difference in the length of the fibres eventually obtained.

Acknowledgment

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The authors wish to express their thanks to Imperial Oil Limited for permission to publish this paper.

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Abstract:—An abstract of not more than about 200 words, indicating the scope of the work and the principal findings, is required.

Illustrations

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